THE MINERALOGICAL MAGAZINE

AND

JOURNAL OF

THE MINERALOGICAL SOCIETY

No. 162 September, 1938 Vol. XXV

The potash-soda-felspars.
II. Some applications to petrogenesis.

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[Read January 28, 1937.]

Contents.

	PAGE
I. The origin of the microcline of pegmatites	87
II. The temperatures of crystallization of the potash-soda-felspars	90
III. The alkali-felspar equilibrium diagram	92
(*a*) The exsolution curve	94
(*b*) The solidus-liquidus curve	95
(*c*) Application of the thermal diagram to granite magmas	97
(*d*) The composition of granite-pegmatites	99
(*e*) Cause of the potassic enrichment of granite-pegmatites	100
(*f*) Immiscible potash- and soda-rich magmas	101
(*g*) Diagram illustrating liquid immiscibility	103
IV. Quartz-microcline graphic structures	105
V. The origin of 'vein' perthite	106
VI. Effects of pressure on the exsolution curve	108
VII. High-temperature pegmatites	110
VIII. Syngenetic felspars formed by solid diffusion	111
IX. Summary	114
X. List of works to which reference is made	116

IN the first part of this paper (33) the effects of heat on the potash-soda-felspars were considered, and a possible explanation in terms of atomic rearrangement was proposed. In this part the experiments, and deductions from them, will be applied to some questions of petrogenesis and differentiation, particularly in connexion with the granites and granite-pegmatites.

I. The origin of the microcline of pegmatites.

In the high-temperature pegmatites, such as those of Fredriksvärn and the moonstone-pegmatites of Ceylon and Burma, the potash-soda-

felspar occurs as anorthoclase or microperthitic orthoclase.[1] In the granites, crystallized probably between 750° and 950° C., this felspar occurs sometimes as microperthitic orthoclase and sometimes as microcline, but in the granite-pegmatites, formed within the temperature range of 500° to 750° C., it appears almost invariably as microcline. In the hydrothermal temperature region below 400° C. only adularia is produced.

Why should crystallization in the 500° to 750° C. temperature region favour the formation of the triclinic form? Warren (41, p. 148), who observed the persistence of microcline and the absence of orthoclase in the granite-pegmatites, introduced an 'inversion' point into the equilibrium diagram to account for the change in form from orthoclase to microcline. According to his interpretation the inversion is probably accompanied by a reduction in solubility for the albite-component, with intensified perthitic exsolution. The inversion makes no provision for the lower-temperature, monoclinic adularia.

The suggestion of Mallard (26) and Michel-Lévy (27) that orthoclase may be a pseudo-monoclinic, sub-microscopically twinned form of microcline avoids the necessity for inversion points. The production of the ordinary coarsely twinned microcline form instead of the pseudo-monoclinic 'orthoclase' form in granite-pegmatites could then be explained by molecular disturbance set up during simultaneous crystallization and exsolution. Against this view of pseudo-monoclinic symmetry are a number of facts already brought out in the first part of this paper, which may be summarized as follows:

1. The orthoclase-microperthite felspars provide an unbroken series which by heat-treatment can be converted into corresponding members of the sanidine-anorthoclase series. The assumption of a sub-microscopic twin-structure for any of these felspars would have to apply to all of them. It is highly unlikely that sanidine, with its optic axial plane parallel to (010), is sub-microscopically twinned, and therefore it is equally improbable that any are.

2. The optic axial angle of orthoclase-microperthite increases with increasing soda-content and lower equilibrium temperatures. The lowest-temperature orthoclases have a smaller optic axial angle than microclines of corresponding composition. This difference cannot be

[1] A number of these soda-rich felspars (Fredriksvärn soda-orthoclase, Berkum anorthoclase, &c.) have sometimes been referred to microcline, but specimens of them which I have examined do not show microcline twinning, but a 'cross-hatching' due to microperthite.

due to relative coarseness of lamellar twinning in the microcline, since the optic axial angle of the latter is already 'averaged' over a large number of microscopic twin-lamellae, and any further subdivision would not alter this average value appreciably.

3. The solubility of the soda-component in ordinary microcline is less than in orthoclase. This would not be so if the felspars differed merely in the fineness of multiple twinning.

4. By prolonged heating, microcline can be converted to the sanidine form. This change is much more difficult to bring about than in members of the orthoclase-microperthite series of corresponding composition.

These observations indicate a fundamental difference between orthoclase and microcline, and support Warren's hypothesis of inversion, rather than the hypothesis of pseudo-monoclinic symmetry in orthoclase.

In the light of experiments described in the first part of the paper, and of recent interpretations of felspar structure, the formation, in some cases of orthoclase, in others of microcline, might be explained as follows. High-temperature crystallization and rapid cooling produce sanidine and anorthoclase forms, monoclinic or almost monoclinic in character even when containing some 50 % of soda-component. In these the sodium-ion fulfils essentially the same function as the potassium-ion in the tetrahedral structure. Of the three principal properties which distinguish albite from orthoclase, viz. refractive index, oblateness of indicatrix, and triclinic symmetry, only the refractive indices are altered slightly towards albite by the inclusion of 50 % of sodium-ions in the anorthoclase structure at high temperatures.

At temperatures of formation down to 850° C. the felspar is still monoclinic and homogeneous (with up to 30 % of soda-component), but the oblateness of the indicatrix and the optic axial angle have increased considerably. This is due in part to the sodium, and in part to the potassium-ion. It may be assumed that this increase in oblateness, which is accompanied by a decrease in the mutual solid solubility of the two felspars, represents a tendency toward a true triclinic symmetry of the soda- and (by analogy) of the potash-component.

In the felspars formed near 850° C., the sodium-ions produce the same oblateness of indicatrix in the homogeneous felspar as they do when separated at lower temperatures in perthite lamellae. On exsolution, the density and refractive index of the soda-felspar lamellae increase to the albite figure, but true triclinic symmetry is apparently not

attained.[1] It seems that soda-felspar of exsolution origin can only take on true albite symmetry when the potash-felspar host at the same time takes on triclinic microcline symmetry. This appears to be possible only when the oblateness of the indicatrix of the potash-felspar is at, or near, a maximum.

When, as in the granite-pegmatites, crystallization falls within the exsolution temperature range of 450° to 750° C., the oblateness of the indicatrix of the potash-felspar is probably near the maximum. Under these conditions albite and potash-soda-felspar are often separating simultaneously from the same magma, while exsolution takes place in the potash-soda member on a slight fall in temperature. This, in the writer's view, represents the optimum condition for the formation of the microcline form.

For still lower crystallization temperatures in the hydrothermal region, the oblateness of the indicatrix would be such that microcline might form, but the necessary disturbing conditions would not usually be present, with the result that the monoclinic form adularia is commonly produced. Alling (1, p. 267) has suggested that the process of grinding sections might cause the inversion of adularia to microcline. The behaviour of adularia toward heat-treatment places it nearer to the microclines than to the orthoclase-microperthite series.

II. The temperatures of crystallization of the potash-soda-felspars.

If we assume that the microperthitic felspars were originally homogeneous and that they held the maximum amount of soda-component in solution at their crystallizing point, the temperature at which they now become homogeneous is probably that at which they were formed, if the effects of pressure can be neglected (see later). In the case of soda-poor felspars formed in potash-rich magmas, the temperature of formation may be somewhat higher than that at which the perthite is redissolved.

The probable crystallizing temperatures of various potash-soda-

[1] The perthite films show no signs of lamellar twinning, while sections on (001) of the felspar, as a whole, show straight extinction. Sections on (001) show a symmetrical interference-figure. It may be that these lamellae represent the monoclinic form of soda-felspar (barbierite). If so, this form is more common than has generally been supposed. Barth (6) has described an antiperthite from Seiland the soda-felspar groundmass of which is uniform and shows straight extinction on (001); but certain parts of the same crystal show slightly oblique extinction and evidence of sub-microscopic lamellar twinning.

felspars are set out in the table below. For completeness, soda-rich representatives are included although knowledge of their temperature of formation is less certain.

Temperatures of formation.	High potash.	High soda.
1100° to 950° C.	40 to 60 % soda-felspar. On slow cooling from high temperatures—schillerized felspar of Burma moonstone type. Sanidine and anorthoclase when more quickly cooled.	Over 70 % soda-felspar. (Usually with some lime.) Oligoclase when slowly cooled. Soda-anorthoclase when rapidly cooled.
950° to 750° C.	25 to 40 % soda-felspar. The common microperthitic orthoclase with high optic axial angle and schiller.	Over 80 % soda-felspar. Some albite-oligoclase.
750° to 400° C.	10 to 25 % soda-felspar. Mainly microclines, with some medium-soda, high-optic axial angle moonstone - orthoclase - microperthites.	Over 85 % soda-felspar. Pegmatitic albite-oligoclase.
400° C. and below	0 to 15 % soda-felspar. Adularia.	Over 90 % soda-felspar. Hydrothermal albite (cleavelandite).

Some true orthoclases, lower in soda than microcline or adularias, e.g. yellow orthoclase and Burma colourless of the first part of this paper, have probably been formed at relatively high temperatures and possibly high pressures, from magmas very poor in soda.

From field and petrological evidence Vogt (37, pp. 64–68) deduced the crystallizing temperatures of various potash-soda felspars to be as follows:

	Percentage of soda-component:	
Temperature.	Orthoclase type.	Albite type.
About 1000–1050° C.	About 60 %	About 68 %
„ 850° C.	„ 32	„ 89
„ 750° C.	„ 27	„ 93
„ 350° C.	„ 14	„ 97
„ 15° C.	„ 9	„ 98

It will be seen that the results of the heat-treatment experiments lead to figures similar to Vogt's and afford an independent check on estimates of the temperatures of formation of rocks containing these felspars.

III. The alkali-felspar equilibrium diagram.

Many attempts have been made to explain the crystallization of the potash-soda-felspars by means of the binary equilibrium diagram.[1] Vogt (35, p. 485) and Warren (41, p. 148) concluded from a study of granites and granite-pegmatites that the equilibrium diagram was of Roozeboom's type V, with a wide immiscibility gap and a eutectic point at about 60 % soda-component. Mäkinen (24, p. 148), from a similar study,

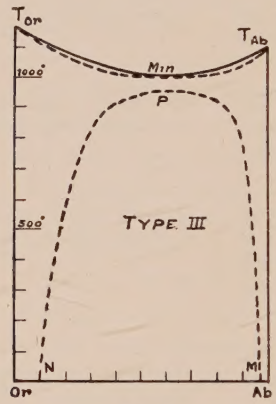

Fig. 1.

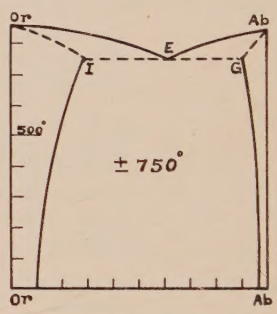

Fig. 2.

Alkali-felspar equilibrium diagrams.
After J. H. L. Vogt, 1926 (37, pp. 88, 91).

made the immiscibility gap much smaller, and the eutectic at about 70 % of soda-component. Dittler (13), from experiments on the melting-points of alkali-felspar mixtures, decided that orthoclase and albite crystallized according to Roozeboom's type III diagram, with a minimum and no eutectic.

Alling (2, p. 289) suggested that these divergent views might all be more or less true for different conditions of crystallization. He combined the various diagrams into a solid model, with an immiscibility gap that increased towards the low-temperature (pegmatitic felspar) end. Similarly, Vogt (37, pp. 88–91) has suggested a number of diagrams

[1] In this discussion the incongruous melting of low-soda orthoclase into leucite and silica as described by Morey and Bowen (28) is ignored. Silica in excess sufficient to prevent the formation of leucite is always present in the rocks under review. The more recent ternary diagram of Schairer and Bowen (29), with excess silica as a third component, is referred to later, see page 98.

ith increasing immiscibility gaps at progressively lower temperatures. or the highest temperatures, in the absence of fluxes, he takes Dittler's olidus-liquidus curve as most probably correct (fig. 1). For the tempera- ure 750° C., with fluxes and mineralizers present, his diagram has a very ide immiscibility gap (fig. 2).

The effect of fluxes and mineralizers must be to depress the solidus- quidus curve along its whole length, and not merely in the eutectic

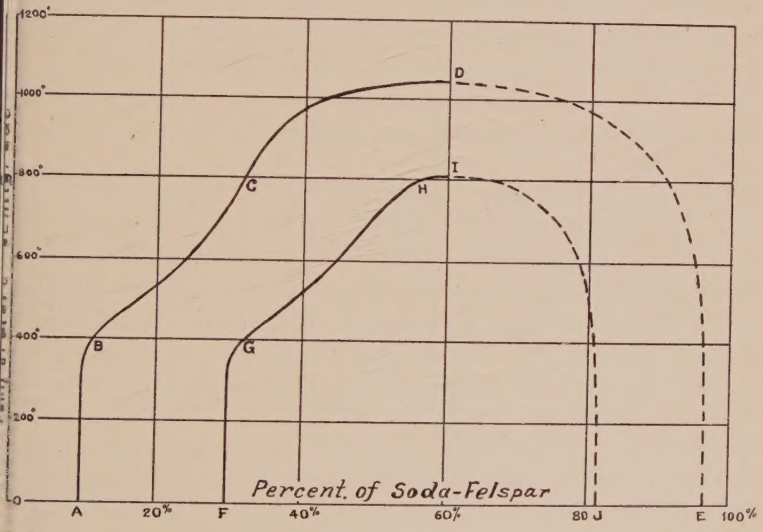

FIG. 3. Exsolution curves for normal and subnormal potash-soda-felspars.

egion. This general lowering of the crystallizing temperature is not, f course, unique. A similar effect is produced in the plagioclase- elspars, but here the lowering of the crystallization temperature has o serious effect on the equilibrium diagram, as complete solid solubility f the two components is maintained down to ordinary temperatures. Vith the alkali-felspars, however, the depression of the solidus-liquidus urves causes them to meet and intersect the exsolution curves at uccessively lower and lower temperatures, giving rise to an increase in ne immiscibility gap, and a corresponding decrease in the amount of olid solution (and ultimately of perthite) in the crystallizing phases.

The factors that affect the solidus-liquidus curve have little direct ffect on the exsolution curve, and vice versa. The two parts of the iagram may be considered separately.

(a) The exsolution curve.

From the experiments of Warren and of Kôzu and from a study o the range of composition of alkali-felspars in igneous rocks, Vogt (37 pp. 64–91) deduced that the exsolution curve of fig. 1 is smoothly convex The experiments described above indicate a relatively sudden change in the solubility of the soda-component in the 350–750° C. temperature range. The curve of fig. 3 (p. 93) shows the flexure due to an increase in the solubility of perthite at 400–500° C., and a decrease at 700–800° C. Heat-treatment experiments have indicated that for temperatures higher than 800° C. and up to the fusion-point of the felspar concerned further solution of perthite takes place at a much slower rate. This is generally accompanied by a reduction in the size of the optic axial angle.

The upper curve of fig. 3 is for normal felspars, formed either by very slow cooling from high temperatures, or by crystallization at lower temperatures with complete equilibrium of optic axial angle and perthite formation. *FGH* represents the exsolution curve for 'subnormal' felspars formed at high temperatures and rapidly cooled (e.g. the Berkum anorthoclase). The incomplete equilibrium caused by rapid cooling[1] is shown in the smaller optic axial angle and reduced oblateness of the indicatrix, while the amount of exsolution is less than in corresponding normal forms. For more rapid cooling, as with some sanidines, and the artificially sanidinized felspars, the optic axial angle is still lower, and exsolution does not take place. It follows that Vogt's diagram (fig. 1), which combines Roozeboom's type III solidus-liquidus curve with the ordinary exsolution curve, can only hold for very high temperatures of crystallization, combined with extreme slowness of cooling.

It was shown above that, by heating perthitic felspars to 800–850° C. and cooling them rapidly, homogeneous metastable forms with 'normal' optic axial angles could be produced, to which the exsolution curve *ABCD* does not apply. Even in volcanic rocks such rapid cooling does not occur. All natural potash-soda-felspar with 'normal' optic axial angles must be completely perthitic to the extent of the exsolution curve *ABCD*.

It follows that, for the potash-soda-felspar series in general, the exsolution curve is not dependent on the cooling rate through the

[1] The term 'rapid' is used here in a relative sense to mean sufficiently rapid to produce felspars with low optic axial angles, and is contrasted with the slower cooling (of deep-seated rocks) which would produce felspars with high optic axial angles.

exsolution temperature range, but on modifications in the atomic structure, which are determined by the cooling rate in the higher temperature regions.

The main difference in the form of the curve *ABCD* from that of Vogt (fig. 2) is the flexure of *ABCD* at 400–800° C. The form of the exsolution curve for 60–100 % soda-component is at present largely conjecture. It has already been suggested (Part I, p. 490) that true potash-soda-felspar representatives in the 60–80 % soda-component region may not exist, but until further information is available one may accept Vogt's continuation of the curve for normal felspars over this region.

(*b*) *The solidus-liquidus curve.*

For high-temperature crystallizations, with fluxes and mineralizers scarce or absent, we may take Dittler's curve (fig. 1) as approximately correct. The depression of this curve by fluxes should be more or less uniform over the felspar field. The intersection of the solidus-liquidus curve with the exsolution curve at successively lower temperature levels down to 800° C. is shown in fig. 4 (p. 96). Below 800° C. it is possible that other factors come into play; this part of the diagram will be discussed later in connexion with the potassic enrichment of granite-pegmatites.

If we regard the fluxes and mineralizers (including the water and excess silica) as equivalent to the third component of a ternary mixture, the falling temperature levels of fig. 4 would be produced from successive parallel vertical sections of the solid ternary-component model, starting with pure alkali-felspars and progressing in the direction of increasing amounts of flux-component as more and more felspar (and silica) are removed by crystallization.

The point *C* of fig. 4 which normally represents the lowest melting-point mixture or eutectic of a binary system, now becomes, on the model, a line along the bottom of a falling valley, for which Vogt (39, p. 411) has suggested the term 'cotectic'. He assumes that the cotectic ratio between the potash- and soda-felspars remains constant at about 40 : 60 %, as the immiscibility gap increases with decreasing crystallization temperatures and increasing quantities of mineralizers. The accumulated evidence of the alkali-felspar-bearing rocks tends to support this view, at least down to crystallization temperatures of the order of 800° C.

A peculiarity of the binary cotectic diagram for the alkali-felspars is that it allows the possibility of changing composition with falling

temperatures, although the cotectic ratio of the magma remains constant. Thus crystallization through the temperature range T_1 to T_2 would produce potash-soda-felspars of gradually changing composition from R to N (about 38 to 32 % of soda-component) together with soda-felspars of S to U composition. Meanwhile the felspar ratio in the remaining magma would be constant at CC_1, with 60 % of soda-component.

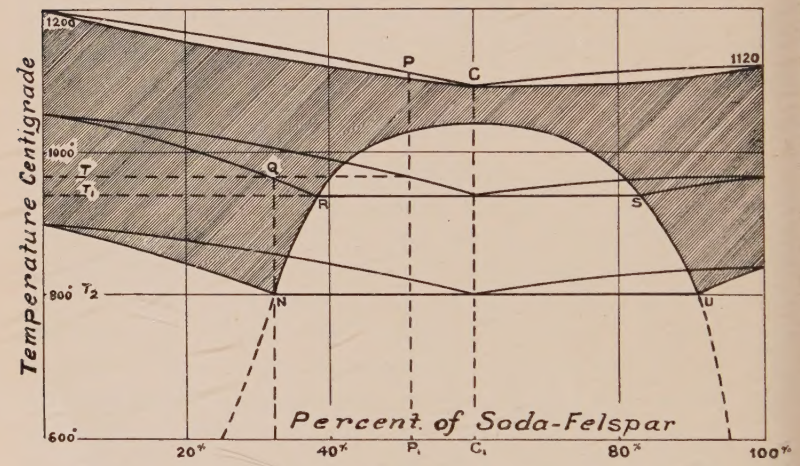

FIG. 4. Suggested cotectic diagram for potash-soda-felspars for temperatures down to 800° C.

These compositional changes in the crystallizing felspars proceed in the opposite direction from those which usually produce phenocrysts by the removal of the component in excess of the eutectic or cotectic ratio. For example, a magma having the initial composition of PP_1 and with sufficient fluxes and mineralizers to form a first cotectic at a temperature T_1, would begin to form phenocrysts of potash-soda-felspar of composition Q at a temperature T. As the temperature fell towards T_1 successive crystallizations would follow the composition line QR with increasing soda-content. Any further drop in temperature below T_1 would be of the cotectic type, with simultaneous crystallization of potash-rich and soda-rich members, as indicated above. The potash-rich crystals separating would now follow the composition line RN with decreasing soda-contents, as the temperature fell from T_1 to T_2.

(c) *Application of the thermal diagram to granite magmas.*

In his first thermal diagram for potash-soda-felspars, Vogt (35, p. 529–535) fixed the eutectic ratio for granitic rocks at 42 % potash-felspar, and the immiscibility gap between 12 and 72 % of that component. In his latter publications the immiscibility gap is made to depend on the 'cotectic' crystallization temperature and the amount of silica and fluxes present, but the same cotectic ratio is maintained, only slightly modified by the presence of much anorthite. Vogt believes that granite magmas have been derived from more basic magmas by differential crystallization (following the thermal diagrams) with the residual felspars tending towards the cotectic ratio as crystallization proceeds (38, pp. 230–241).

Bowen (10) arrives at similar conclusions from the experimental evidence obtained from the ternary equilibrium systems. He shows that dry melts containing free silica and an alkali alumino-silicate, with lime, magnesia, or iron as the third component, become, by a process of fractional crystallization, enriched in alkali alumino-silicates. The same process acting on a mixture of all these components would concentrate the alkali alumino-silicates in the residual liquid, thus tending towards the ternary system $NaAlSiO_4$–$KAlSiO_4$–SiO_2, which Bowen considers to be the 'residua' system of petrogeny. The equilibrium diagram for this system by Schairer and Bowen (29) is reproduced in fig. 5 (p. 98). Bowen regards the oblong belt or trough of low melting temperatures (*abcd*) as a 'sink' towards which the alkali alumino-silicate-silica residues of rock magmas tend to converge. Most phonolites, trachytes, and rhyolites, when reduced to an alkali alumino-silicate-silica basis (and they usually contain well over 80 % of these constituents) lie within the belt (*abcd*), and the same applies to many syenites and granites. These rocks have crystallized at temperatures well below the lowest isotherms of fig. 5 and their position in the 'sink' indicates that the depression of the melting-point surfaces by fluxes and mineralizers has not caused the cotectic lines appreciably to deviate.

The potash-granites, however, lie well outside the 'sink', just as they lie on the *wrong* side of the cotectic line of Vogt. Bowen (9, pp. 227–231) accounts for these by assuming that the relation between orthoclase and anorthite is not of the eutectic kind, but a 'reaction' with no minimum.[1]

[1] The formation of mantles of orthoclase around basic plagioclase, which Bowen considers to be due to a 'reaction' process, may possibly be due to other causes, e.g. supercooling. The reverse arrangement of oligoclase borders to orthoclase (rapakiwi granite, &c.) is definitely not a 'reaction' relationship.

As a consequence he makes the Or, Ab, An cotectic line lie nearer the Or–Ab side than does Vogt. Doggett (15), from a consideration of many rock analyses, also makes the cotectic line lie nearer the orthoclase-albite join.

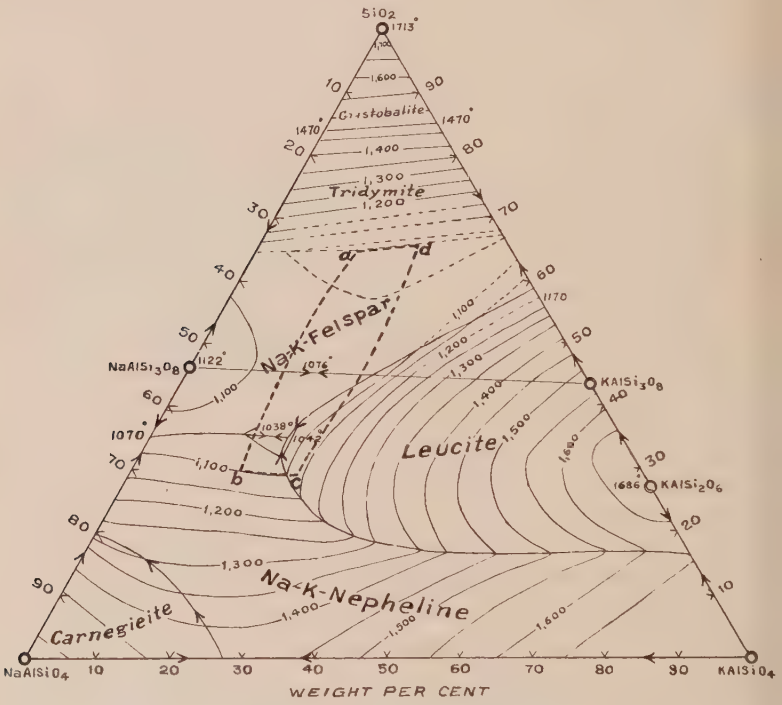

Fig. 5. Equilibrium diagram of the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2. After J. F. Schairer and N. L. Bowen, 1935 (29, p. 326).

Vogt (38, pp. 220–229) has criticized these views, pointing out that, according to Bowen's diagram, orthoclase could crystallize before plagioclase only over a very limited range of composition, whereas, in potash-granite, orthoclase occurs as primary phenocrysts over a much wider range. He holds that these highly potassic granites have been produced by myrmekitization and late stage magmatic reactions within the more basic magmas, before a separation by 'filter-pressing'.

Recently, Doggett (16) has pointed out that such reactions would involve a departure from Vogt's binary diagram, and suggests that a deviation of the cotectic line towards the potash side with increasing

amounts of fluxes might explain the potassic enrichment. It is suggested that this is implied in Vogt's discussions of these magmas, although his various cotectic diagrams (37, pp. 88–91) with nearly constant felspar ratio are at variance with this view.

Whatever their origin, these potash-rich rocks provide perhaps the best example of crystallization according to the normal binary diagram with immiscibility gap, i.e. the excess potash has been eliminated as phenocrysts of orthoclase or microcline, while the composition of the residual magma has moved toward the 40:60 potash:soda-felspar ratio. It follows that either of the above explanations (myrmekitization, or a deviation of the cotectic line) could represent only a temporary aberration of the normal sequence of crystallization, and it does not seem possible that with gradually falling temperatures the sequence could oscillate in this manner, or vary so abruptly without apparent cause.

(*d*) *The composition of granite-pegmatites.*

The origin of the granite-pegmatites is even less satisfactorily explained by the thermal diagram than is that of the potash-rich granites. Derived from the residual magmas of the granites with which they are associated, the pegmatites, according to Vogt's diagram, should have a composition closer to the cotectic ratio than the parent granite, whereas they are usually more potassic.

Owing to the very coarse character of most granite-pegmatites, few *average* chemical analyses are available, but there is much evidence to show that they are predominantly potassic rocks. For instance, descriptions and statements by Vogt (38, pp. 68–73), Mäkinen (25), Derry (12), and Fersman (18) all emphasize the dominantly potassic nature of these rocks. Landes (23, p. 96) states that the volume of the complex albite-bearing pegmatites is almost negligible in comparison with that of the 'simple' quartz-microcline-muscovite type.

Granite-pegmatites examined by the writer in many localities in India also show this preponderance of potash-soda-microcline. For instance, in the Kodarma mica-mining area, Bihar, pegmatites occur both in a granite-gneiss ('dome-gneiss' of the Survey) and in the country schists. In the gneiss occur quartz-microcline-muscovite-pegmatites with subordinate albite-oligoclase, corresponding to the 'simple' pegmatites of Landes. The microcline usually consists of mixtures of 'film' and 'vein' perthite; in some cases it is graphically intergrown with quartz, but in others it is coarsely crystalline and idiomorphic. Where albite-oligoclase occurs in these 'simple' pegmatites, it seems to have crystallized

idiomorphically before the quartz-microcline graphic structures. It never occurs as a ternary eutectic. Thus the tendency of the residual potash-rich pegmatite magma is towards a still more highly potassic ratio.

In the country-rocks, both 'simple' and 'complex' pegmatites occur, with predominant microcline and albite-oligoclase respectively. In the former type, microcline, quartz, and muscovite are associated with subordinate albite-oligoclase and varying quantities of biotite, tourmaline, garnet, apatite, and other accessory minerals. The microcline is of the composite 'film' and 'vein' perthite type, sometimes as crystals two or three feet in length. Fine and coarse graphic intergrowths with quartz occur.

The plagioclase-rich pegmatites consist mainly of quartz, albite-oligoclase, and muscovite, with accessory tourmaline, garnet, apatite, and beryl. The albite-oligoclase is sometimes of the hydrothermal cleavelandite variety and is frequently associated with a greenish-yellow mica resembling gilbertite. Quartz, plagioclase, and muscovite are coarsely (and often regularly) intergrown, but no graphic intergrowths of quartz and plagioclase were noted.

Many of the larger pegmatites appear to be mixtures of the above two types; it is probable that the soda-rich portions have been formed by the albitization of previously intruded microcline-quartz-muscovite-pegmatite.[1]

Quantitatively, the Kodarma pegmatites are predominantly potassic, the majority being of the 'simple' quartz-microcline-muscovite type. Where the soda-felspar is present in more than subordinate amounts, it occurs almost to the exclusion of the potash-felspar. There is nothing approaching the 40:60 potash:soda-felspar ratio of Vogt's residual magma.

(*e*) *Cause of the potassic enrichment of granite-pegmatites.*

Vogt (38, pp. 89–91) considers that myrmekitization and late-stage reactions in the residual granite magma followed by 'filter-pressing' would account for the potassic nature of granite-pegmatites. This explanation really involves a modification of the binary felspar diagram. If, as Vogt assumes, this is a temporary modification caused by the special conditions of late-stage crystallization, the removal of the pegmatite magma should be followed by a return to normal conditions of crystallization, with impoverishment in potash, but the field evidence

[1] Cf. Schaller (30, pp. 274–279).

points to a further enrichment in potash during the crystallization of pegmatite.

Doggett's suggestion of a movement of the cotectic line towards the potash side, with increasing amounts of fluxes, has the merit of simplicity. The end of this process would be the formation of quartz-microcline graphic structures, which would represent a ternary cotectic with the 'vein' perthite as the plagioclase component.

Such a deviation of the cotectic line from the 40:60 ratio of the granite residual magma to 70:30 in the final graphic pegmatite would require the removal by crystallization of about 70 % of the original soda-component as albite-oligoclase, either in the granite or the early pegmatite crystallization, or in both. If most of this change took place in the last stages of crystallization of the granite, the average composition of that rock might not be seriously affected because of its relatively large mass in comparison with the residual magma. But the deviation of the cotectic line would then be extremely sharp for such a small drop in temperature. On the other hand, the field evidence does not support the view that any large portion of this excess albite separated in the early stages of crystallization of the 'simple' pegmatites. Moreover, the complex albite-bearing pegmatites demand a late-stage, partly hydrothermal, soda-rich magma, certainly out of keeping with a deviation of the cotectic line to the potash side.

Beskow (8), Goldschmidt (20), and others have accounted for soda-enrichment by the elimination of potash in the form of biotite, instead of, or in addition to, potash-felspar, particularly in water-rich magmas. While this process, and myrmekitization or a deviation of the cotectic line, may have produced soda-rich and potash-rich magmas respectively, they could not have been active at the same time, nor is it likely that one process could have immediately followed the other. Hence we must look for some other explanation of the frequent occurrence of both potash- and soda-rich pegmatites in association with the same granite intrusion.

(*f*) *Immiscible potash- and soda-rich magmas.*

The writer suggests that these apparently conflicting data can be harmonized by assuming that, during the later stages of the crystallization of the granite, the residual magma separated into two fractions of gradually increasing immiscibility, one very rich in soda, the other rich in potash but containing some soda. The latter would represent the magma of ordinary granite-pegmatites.

Liquidity in this temperature region—about 400–1000° C. below the melting-points of the three principal components, and 300–400° C. lower than that of their 'dry' eutectic—is only possible in the presence of considerable quantities of fluxes and mineralizers. Immiscibility in such a magma is a more logical development of the higher-temperature cotectic diagram than a re-solution of orthoclase or a diversion of the cotectic ratio.

It simply means that the rapidly decreasing mutual solubility of the two solid felspar phases—brought about by falling temperature, and possibly accentuated by a change to the microcline form—has extended to the liquid phase. In the same way that at higher temperatures the intersection of the solidus-liquidus with the exsolution curve inhibits the formation of a single homogeneous felspar phase from a magma of binary cotectic composition, so its intersection with the immiscibility curve would prevent the crystallization of the single quartz-orthoclase-albite cotectic, and give rise instead to two separate cotectic magmas.

Assuming that the potash : soda-felspar ratios in the potash-rich and soda-rich phases are of the order of 60:40 and 10:90, the relative proportions of the two phases produced from a magma of cotectic ratio 40:60 would be approximately as three is to two; i.e. the potash-rich phase would be in excess. This partial magma, largely removed by 'filter-press action', would give rise to the 'simple' granite-pegmatites.

The soda-rich magma, smaller in quantity and possibly denser, might follow the channels taken by the potash-rich fluids, to give rise to albitization and the 'complex' pegmatites. It would also tend, in part, to remain between the crystals of the partly consolidated granite, there to give rise to myrmekite, deuteric perthite, and similar structures, which are often regarded as products of late-stage magmatic reaction.

Although many writers (e.g. Sederholm (32), Schaller (31), and Gilluly (19)) have considered myrmekite to originate through secondary replacement, others claim for it an origin in direct crystallization. The Indian charnockites are rich in myrmekite, and my examination of many of them shows that the myrmekite boundary—which is usually curved and sometimes totally enclosed by orthoclase—cuts sharply across the microperthitic structure. This indicates that the myrmekite was formed before perthite exsolution took place, i.e. above 400° C. and probably not below 600–700° C.

Becke (7, pp. 384–390) showed that the amount of quartz in myrmekite increases with the anorthite content of the plagioclase. He suggested

that in the replacement of potash-felspar by plagioclase, silica was liberated in proportion to the amount of lime present in the latter.

The same variation of the quartz would also result from the crystallization of plagioclase from a residual magma rich in soda and lime, if the amount of excess silica and water were controlled by the metallic oxides present, rather than by the felspar ratio. I have found nothing in the Indian charnockites inconsistent with the view that the myrmekite has crystallized directly from an albite-rich phase produced by immiscibility on the lines indicated above.

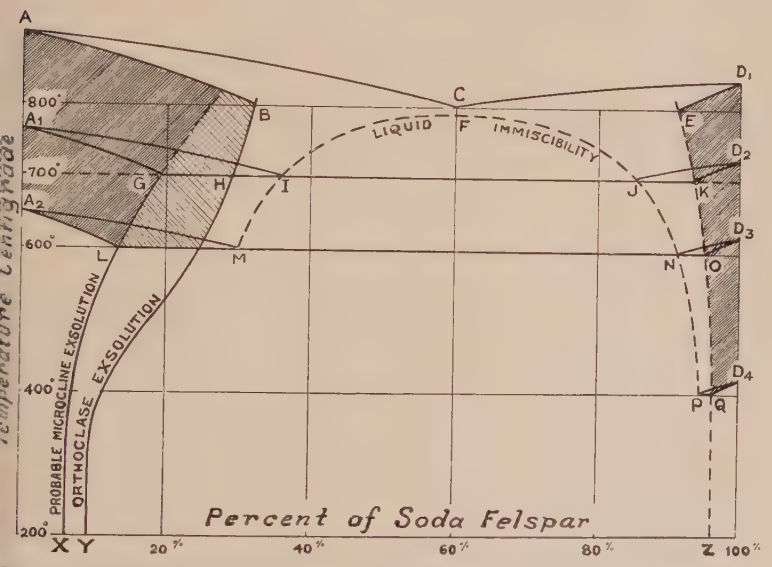

FIG. 6. Suggested cotectic diagram for potash-soda-felspars for temperatures below 800° C.

(g) Diagram illustrating liquid immiscibility.

Fig. 6 extends the thermal diagram of fig. 4 to show liquid immiscibility below 800° C. The curve *MFN* limits the field of complete immiscibility; the exsolution curve for orthoclase below 800° C. is *BHY*, and for microcline, *GLX*. According to this diagram, a magma of cotectic composition at 800° C., if further cooled (with continuous separation of potash- and soda-felspars and quartz), would gradually separate into two immiscible magmas, with the compositions *I* and *J* at 700° C. and *M* and *N* at 600° C.

Consider first the potash-rich magma. The solubility of the soda-

component in the solid potash-felspar at a temperature of 700° C. is represented by H for the orthoclase and by G for the microcline form. There is a tendency in this temperature region for microcline to separate, so the solidus-liquidus curve has the form A_1GIF. When microcline of composition G forms, the magma is enriched in soda by an amount GI. This excess of soda might add to the immiscible soda-magma J, it might form albite-oligoclase of composition near K, or it might form 'vein' perthite within the microcline, depending upon the pressure, the rate of cooling, and the rate of elimination of volatile fluxes. At 600° C., approximately the temperature of final crystallization of the quartz-microcline graphic cotectic, the felspar ratio in the magma corresponds to M and the microcline separating out has the composition L. The microcline in the graphic cotectic would contain up to LM % of albite-oligoclase as 'vein' perthite, depending upon how much is removed as a late-stage hydrothermal albite-rich magma.

The crystallization of the soda-rich fraction would follow similar lines, but the proportion of the potash-component present would be small. Field evidence suggests that the residual portion of this soda-rich magma collects more of the volatiles and nearly all the rare elements, and that it retains fluidity to a considerably lower temperature than does the potash-rich magma.

The above explanation accounts for the narrow range of composition of graphic structures, 'vein' perthite, and true myrmekite better than any theory of origin by replacement. Below a certain temperature, immiscibility would demand the formation of binary quartz-microcline or quartz-plagioclase cotectics, rather than the ternary quartz-microcline-plagioclase cotectic required by the diagrams of Vogt and of Schairer and Bowen. It cannot be accident that these binary cotectics frequently occur in pegmatites, while the ternary cotectic is apparently absent. Granite-aplites, granophyres, and microgranites sometimes approach the latter in composition, but they probably represent rapidly cooled, high-temperature magmas.

Sundius (34) has recorded the occurrence of two types of aplite in association with the Lofthammer granite which he believes to have been produced by immiscibility from a parent granite magma. One type is red and potassic and the other—which occurs in much smaller quantities —is white and albitic. Myrmekitization is common in the granite and in the red aplite. Asklund (5) has also described a granite-norite rock suite in the neighbourhood of Stavsjö, which in his opinion has been developed by a process of liquid separation.

Bowen (9, pp. 13–16) objects to the view that immiscibility has caused differentiation in rock-magmas, partly on the ground of negative evidence, viz. the absence of globules of the differentiate in glassy rocks, and the absence of a discontinuity at the crystallizing surfaces. If liquid separation has occurred, as is suggested here, in the later stages of the consolidation of the granites, the slow cooling and coarse crystallization would obliterate such traces of immiscibility. Nevertheless, it is possible that many 'deuteric' and 'vein' perthites and myrmekitic structures may represent residual portions of immiscible magmas.

Greig (21) has shown that although some of the silicates of lime and magnesia form immiscible mixtures, the silicates of potash and soda are completely miscible. It must be remembered that in the pegmatite magmas we are dealing not with simple silicates, but with alumino-silicates in the presence of excess silica and fluxes at temperatures very much below the dry melting-point. It may be significant that the immiscible systems described by Greig contained high concentrations of silica.

IV. Quartz-microcline graphic structures.

The somewhat narrow range of composition of quartz-microcline graphic structures was first noted by Mäkinen (25, p. 30), who found that the ratio of quartz to microcline varied between 23:77 and 32:68. Vogt (38, p. 125), from a study of the Norwegian pegmatites, concluded that these structures represented the final simultaneous crystallization of a quartz-microcline cotectic in the presence of silica solutions and mineralizers at a temperature of 600–640° C. He refers to Fersman's proof of the simultaneous crystallization of quartz and microcline (17) and shows that quartz, in his own specimens, varies only between 20 and 25 %, with a mean of 23 %, whilst the proportion of (Ab+An) has the same range as that of ordinary pegmatitic microclines.

Five Indian specimens (from Kodarma in Bihar and Jointora in Orissa) of quartz-microcline graphic structures show a slightly wider range of free quartz (15 to 26 %), with an average of 20 %. The microcline averaged 20 % of soda-lime-felspar, with an extreme range of 13 to 31 %. On the whole, these specimens tend to support the view that the structures have a limited compositional range.

Vogt, as mentioned above, considers that these structures are binary cotectic crystallizations. The writer suggests that they represent the last stage of potassic enrichment which began in the separation of the granite residual magma into immiscible sodic and potassic fractions.

Falling temperatures, and changes in the amount of silica and fluxes present, caused the latter fraction to become further enriched in potash, with the final separation of the quartz-microcline graphic structures.

V. The origin of 'vein' perthite.

The coarse, irregular variety of perthite generally associated with the microcline of pegmatites and the finer 'exsolution' perthite were both referred to by Warren (41, p. 129), who considered the coarse 'vein' perthite to be formed by direct crystallization or in the early stages of exsolution, and the finer 'film' perthite during or after the transformation into microcline.

Andersen (4, pp. 149–153), who suggested the term 'vein' and 'film' or 'string' perthite for the two forms, considers that the former may have been produced by the infiltration of albite-bearing solutions into the host felspar, along shrinkage cracks nearly perpendicular to the *a* crystallographic axis. He cites the experiments of Kôzu and Saiki (22) on the thermal expansion of six specimens of potash-soda-felspar. These workers found that the coefficient of expansion in the direction of the *a*-axis between 0° and 1000° C. was greater than in the directions of the *b*- or *c*-axes. The expansion along the *a*-axis was 2 %, while the mean value in the direction of the *b*- and *c*-axes was 0·6 %. A detailed examination of these results gives less support to the hypothesis of shrinkage cracks than Andersen claims. One of Kôzu and Saiki's specimens was adularia, which should be excluded from the present discussion as it has been formed below 400° C. and contains no 'vein' perthite, yet its high expansion ratio of 8:1 has raised the average. Similarly, Ceylon moonstone (also mentioned in the experiments) has an expansion ratio of 6:1, although this and other soda-rich felspars formed at relatively high temperatures show no evidence of shrinkage cracks and rarely contain 'vein' perthite.

In addition, the temperature range through which contraction can have been effective in pegmatitic microcline (the true host of 'vein' perthite) extends only from 750° to 350° C., much less than the experimental range of 0° to 1000° C. This very much reduces the possible volume of shrinkage cracks. Other objections to this view of the origin of 'vein' perthite by replacement or infiltration are as follows:

1. The (Ab+An) content of the microcline which bears 'vein' perthite is never more than about 30 %. If we allow 6 to 14 % for the 'film' perthite invariably present, it is clear that 'vein' perthite can never exceed 20 to 25 %, whereas the maximum possible replacement by soda-

felspar would be about 86 to 94 %. This in itself is strong evidence against a replacement or secondary infiltration origin for the 'vein' perthite.

2. In most specimens the 'vein' perthite is in optical continuity with the microcline, i.e. the albite-twin lamellae of the perthite lie parallel to those of the microcline. One would expect this to be the case if crystallization of the microcline and perthite had been simultaneous, but not necessarily so if the albite were of later infiltration origin.

3. The 'vein' perthite grades in size from about 2 mm. maximum thickness in some specimens to near the dimensions of the 'film' perthite (0·001 mm. thick) in others; when it approaches the latter's regularity of form and distribution. It is doubtful whether infiltration could produce such regularly arranged and finely divided albite films.

4. The widespread occurrence of 'vein' perthite in the microcline of ordinary granite-pegmatites (which usually show no evidence of albitization) is against an origin by replacement.

5. In quartz-microcline graphic structures the 'vein' perthite shows no tendency to follow the quartz-microcline junctions, and ignores the graphic structure, whatever the size of the latter. Shrinkage cracks produced in the microcline on cooling should have fractured the interlocking quartz plates and strings in various places, and so have allowed 'cross-veins' of perthite to form. The 'vein' perthite is never seen to cross the quartz bands in this manner, or even to corrode them. To some extent the size and form of the 'vein' perthite appears to be regulated by the size of graphic structures.

6. There is definite microscopic evidence that the coarseness of the cross-hatch twinning in the microcline has been affected, or regulated, by adjacent 'vein' perthite, and in some cases by adjacent graphic quartz. For secondary albite to produce this effect there must be a concomitant reconstitution of the host microcline. The regularity of the film or exsolution perthite in these areas is against such a reconstitution having taken place.

To overcome these difficulties the writer suggests that 'vein' perthite has been formed by the simultaneous crystallization of the 'vein' albite and the host microcline (together with quartz in the case of the graphic structures). The magma of the simple pegmatites, in which typical 'vein' perthite almost invariably occurs, has been shown (see p. 102) probably to be the immiscible potash-rich fraction derived from an original granite magma. The present explanation of 'vein' perthite suggests that the 30–40 % of soda-component held in solution in this

potash-rich magma, less the amount (6–20 %) in solid solution in the crystallizing microcline, has separated, in the main, simultaneously and in optical continuity with the microcline as coarse albite-oligoclase lamellae, either in the early pegmatitic crystallization, or later in the graphic structure.[1]

If the above explanation is correct, the term '"vein" perthite' leaves something to be desired. Alling's 'eutecto-perthite' is better (3, p. 48), but perhaps the term 'cotecto-perthite' would more correctly express the relations of this variety of albite blebs.

VI. Effects of pressure on the exsolution curve.

It was assumed (see above, p. 90) in discussing the exsolution curve in relation to temperatures of formation, that experimental results obtained at atmospheric pressure could be applied without correction to natural conditions. This assumption may not introduce serious errors for lavas and most pegmatites, but for deep-seated rocks formed under high pressure a correction will be necessary. We have seen that a considerable increase in volume takes place during the solution of microperthite, and it may be inferred that high pressure would tend to reduce the amount of solid solution at any given temperature.

In this connexion consider the Clasius-Chapeyron equation $\delta t/\delta p = 10{\cdot}33\ (V_1 - V_2)\ T/E.Q$, where $\delta t/\delta p$ is the change in melting-point of a solid (in degrees Centigrade) for unit increase of atmospheric pressure. T is the melting-point of the solid on the absolute scale. $(V_1 - V_2)$ is the difference in specific volume between liquid and solid at the melting-point, and Q is the latent heat of solution in gram calories per gram. E is a constant and equals 425. For microperthite solid solutions $(V_1 - V_2)$ may be taken as the difference in specific volume between the two phases of the soda-component, i.e. when it is in complete solid solution in the potash-felspar, and when it is separated as albite lamellae. The specific gravity of pure albite is 2·628 and that of pure orthoclase is 2·588. The specific gravity of the potash-felspar is increased by about 0·002 for every 10 % of soda-felspar dissolved in it. The difference in specific gravity between the dissolved and albite form of soda-felspar is thus approximately $2{\cdot}628 - (2{\cdot}558 + 0{\cdot}020)$, and the value of $(V_1 - V_2)$ becomes $2{\cdot}628 - 2{\cdot}578/2{\cdot}628 \times 2{\cdot}578$ or very nearly 0·008.

The value of Q is at present undetermined. Dittler and Köhler

[1] This does not preclude the occurrence of 'vein' perthite of secondary origin, but it does suggest that the commonly occurring, regularly arranged 'vein' perthite of granite-pegmatites is a contemporaneous product.

(14, p. 260) tried to measure the heat of solution of perthite by a differential method, but without success. It is probable that Q will be of the same order of magnitude as the latent heat of inversion of α- to β-quartz, which, according to Wright and Larsen (42), is about $4{\cdot}3 \pm 1$ calories. For calculation we may assume that Q is 5 calories per gram at the crystallizing temperature of 800° C. $\delta t/\delta p$ then becomes $10{\cdot}33 \times 1073 \times 0{\cdot}008/425 \times 5 = 0{\cdot}0418$. This implies a rise in the temperature of exsolution of about 40° C. for a pressure of 1000 atmospheres, which is of a higher order than that calculated by Vogt (36) for the rise in the crystallization temperature of rock magmas, viz. 4° to 10° C. for 1000 atmospheres.

Thus, for deep-seated rocks, where pressures of the order of 10,000 atmospheres may occur, the modification of the exsolution curve will be large. The final effect will be to raise that part of the curve between 10 and 40 % soda-component into the higher temperature region, and at the same time make the slope steeper. As a result, phenocrysts will form with less soda-component—for a given crystallization temperature—than is shown by the exsolution curve of fig. 3. At the same time conditions will be less favourable to the formation of the microcline form because of the reduced amount of exsolution and the less oblate form of the indicatrix of the crystalline felspar.

How far does petrological evidence support these conclusions? If, as Vogt estimates, granites have crystallized between 950° and 800° C., the amount of soda-component in the potash-felspar should be of the order of 30 to 40 %, assuming the crystallization to have taken place under atmospheric pressure. But many porphyritic granites contain phenocrysts with distinctly lower soda-contents than this, even when the potash-soda-felspar content of the rock approaches the 40:60 cotectic ratio. As instances, we may consider Dartmoor granite, with phenocrysts approximating to $Or_{71}Ab_{27}An_2$; Shap granite, with phenocrysts of $Or_{73{\cdot}5}Ab_{24}An_{2{\cdot}5}$;[1] and Peterhead quartz-porphyry, with phenocrysts of $Or_{79}Ab_{20}An_1$. The porphyritic felspars of these three rocks are orthoclase-microperthites.

The garnetiferous gneissose granite of Kalahandi, Orissa, India, from which specimen E (see tables I and II, Part I) was obtained, provides another good example. This rock is exposed intermittently over a belt of country some 16 miles wide by at least 100 miles long (Walker, 40,

[1] Vogt (38, p. 203) refers the Shap phenocrysts to microcline, but specimens which I have collected and examined show no trace of cross-hatch twinning on (001), while the optic axial angle (2V 60°) is that of normal perthitic orthoclase.

pp. 6–7). Samples collected by me contain up to about 30 % of fresh microperthitic orthoclase phenocrysts, several inches across, and usually in the form of Carlsbad twins. The groundmass consists of plagioclase, orthoclase-microperthite, garnet, and biotite, with hypersthene and quartz as accessories. The composition of the plagioclase is approximately $Ab_{45}An_{55}$.[1] Sufficient soda is present to ensure the saturation of the early-formed orthoclase phenocrysts, yet they contain only 14 % of this component. Analyses of the rock, and of the matrix, freed as far as possible from the porphyritic felspars, are given below.

	(*a*)	(*b*)
SiO_2	63·78	61·90
TiO_2	1·17	1·60
Al_2O_3	16·21	15·00
Cr_2O_3	nil	nil
Fe_2O_3	0·60	1·04
FeO	4·93	8·06
MnO	0·11	0·19
MgO	1·27	2·22
CaO	3·84	5·21
SrO	nil	n.d.
BaO	0·20	n.d.
Na_2O	1·82	1·68
K_2O	5·16	2·18
H_2O+110° C.	0·46	n.d.
H_2O−110° C.	nil	n.d.
CO_2	0·05	n.d.
SO_3	0·08	n.d.
P_2O_5	0·25	n.d.
Cl	0·017	n.d.
Total	99·95	99·08

(*a*) Garnetiferous granite-gneiss. From railway cutting and quarry near Ombadowla, Kalahandi State, Orissa, India.

(*b*) The matrix of the above rock, after the removal of the porphyritic felspars. Same locality.

All chemical analyses given in this part and in the first part of the paper are by E. Spencer and K. B. Sen, unless otherwise stated.

VII. High-temperature pegmatites.

Although most pegmatites have probably crystallized between 500° and 800° C., field and laboratory evidence both suggest that the soda-rich felspars of the Ceylon moonstone pegmatites, the Mogok, Burma, gemstone pegmatites, and the Fredriksvärn pegmatite must have crystallized at higher temperatures. The exsolution curve *ABCD* of fig. 3

[1] I am indebted to Mr. W. D. West of the Geological Survey of India for this determination of the plagioclase on the universal stage.

shows that felspars of these compositions (about 30 to 50 % of Ab+An) must have been formed at not less than 900° C.: even low pressures would raise the temperature to the order of 1000° C. for the more sodic forms.

The common association of these pegmatites with gemstones such as ruby, sapphire, zircon, and spinel, the very small quantities of ferromagnesian minerals present, the relatively small proportion of free quartz, and the almost complete absence of mica all point to the presence of only small quantities of fluxes and to a high temperature of formation.

VIII. Syngenetic felspars formed by solid diffusion.

The potash-soda-felspars described in this paper all belong to rocks of magmatic origin. This is indicated by their field relationships and by their behaviour to heat-treatment. Except for one or two microclines which show a little 'vein' perthite, all the specimens can readily be made homogeneous by heating, and were undoubtedly so at the time of their formation.

There are, however, alkali-felspars which were not formed by crystallization from a magma. Apart from the authigenous felspars formed in unaltered, or only slightly altered, sedimentary rocks, there is much to show that felspars may form under conditions of thermal metamorphism at temperatures below the melting-points of any of the rock constituents.[1] One strong line of evidence is the common occurrence of phenocrysts (porphyroblasts) of potash-soda-felspar in semi-pelitic xenoliths, sometimes when the latter still retain their original bedding or schistosity, showing that the xenolith remained solid.

The composition of the xenoliths precludes a simple origin by molecular reconstitution for the felspar porphyroblasts. It is possible that the silica and alumina may have been more or less in situ, but the potash and soda must have been locally concentrated by migrating solutions or by solid diffusion. The second process may in some ways resemble the migration of ions referred to in connexion with the formation of perthite (see Part I, p. 485). If this latter view is correct, the silico-alumina framework in certain parts of the xenolith may have acted as a one-way 'sink' towards which any potassium or sodium ions would migrate to form an alkali-felspar structure.

These porphyroblasts must have been formed in a relatively short time as compared with the total time of magmatic consolidation and metamorphic action. It is possible that the same process acting over long periods might produce holocrystalline rocks with more or less com-

[1] See, e.g., A. Brammall (11, pp. 97–98.)

plete obliteration of the original structure, without the mass having reached even a plastic condition. How far such a process might have given rise to granitic and similar rocks is outside the scope of this discussion, but it might be worth while to consider the characters of alkali-felspars formed under such conditions.

One would expect such crystals to be less homogeneous than those formed from magmas, owing, firstly, to unassimilated non-felspathic material, and secondly, to the lessened mutual solubility of the two felspars at lower temperatures. Any excess of soda-component, for example, over the composition represented by the solid saturation point for that particular formation temperature, would form parallel growths or some crude form of perthitic structure, easily distinguishable from exsolution perthite, or regular 'vein' perthite. Microperthite of exsolution origin would be of less frequent occurrence than in felspar formed from magmatic crystallization, but where found, the composition should correspond to the exsolution curve for the particular formation temperature.

The large felspars in xenoliths in the Shap granite, many of which I have examined, show the same homogeneous structure (with fine exsolution perthite) as do those of the surrounding granite. One crystal was found to have an optic axial angle 2V 61°, the same as those of phenocrysts from the granite. In chemical composition the felspars of the granite and of the xenoliths are almost identical (see analyses below).

	(*a*)	(*b*)	(*c*)
SiO_2	64·60	64·28	68·58
TiO_2	—	—	0·66
Al_2O_3	19·38	19·40	14·34
Fe_2O_3	0·22	0·34	2·00
FeO	—	—	2·34
MnO	—	—	0·23
MgO	trace	trace	1·58
CaO	0·28	0·48	1·68
Na_2O	2·78	2·74	3·04
K_2O	11·78	11·80	4·80
$H_2O+110°$ C.	—	—	0·34
$H_2O-110°$ C.	—	—	0·15
CO_2	—	—	0·06
Loss	0·70	0·58	—
Total	99·74	99·62	99·80

(*a*) Orthoclase porphyroblast from semi-pelitic xenolith in granite. Shap quarry, Westmorland. $Or_{69·62}Ab_{23·50}An_{1·40}$.

(*b*) Orthoclase phenocryst from Shap granite, Shap quarry, Westmorland. $Or_{69·74}Ab_{23·16}An_{2·40}$.

(*c*) Porphyritic granite (adamellite). Shap quarry, Westmorland.

Some of the porphyroblasts show an oscillatory zoning of the microperthitic structure. Whether these crystals have been formed in situ in the xenolith, or have been introduced bodily from without, it is clear that their temperature of formation has been very little lower, if at all, than that of the associated granite magma, and certainly not lower than that at which orthoclase of composition $Or_{74}Ab_{24}An_2$ becomes homogeneous, i.e. not less than about 700–800° C.

Another specimen, kindly supplied to the writer by Dr. A. Brammall, is a xenolith of Malmesbury shale in the Kloof granite, Cape Town. This xenolith has a banded structure and a dark grey colour, and contains porcelain-white felspars up to one and a half inches across. Some of the crystals have incompletely formed outlines and most of them contain unassimilated non-felspathic material. One large crystal was found to have the composition $Or_{70}Ab_{27}An_3$. It was too heterogeneous for refractive index determination, but a fairly clear fragment had an optic axial angle of about 2V 77°.

Sections on (010) display a coarsely perthitic arrangement of potash- and soda-felspar much more irregular than the usual 'vein' perthite. In addition, a very fine exsolution microperthite is visible in the potash-rich areas. Sections on (001) show the same coarse, irregular perthitic structure, and also evidence of the cross-hatching of microcline.

The presence of microperthite of exsolution origin in these porphyroblasts shows that they were formed at a temperature above 400° C. On the other hand, the presence of unassimilated, coarsely perthitic albite-oligoclase indicates a formation temperature lower than that of the crystallization of granite magmas. The amount of soda-felspar present as coarse perthite is about 20 %, leaving about 10 % to be accounted for by the fine exsolution microperthite. This suggests that the formation temperature of these crystals has been nearer the lower than the upper limit of the 400–800° C. exsolution temperature range.

Phenocrysts separated from the associated Kloof granite also show similar coarse perthite and unassimilated non-felspathic material, but the coarse perthite is more regular, and apparently smaller in amount, than in the crystals from the xenolith. Exsolution microperthite is visible in the potash-rich areas, which also show microcline twinning.

Sections of the groundmass of the xenolith show a coarsely banded arrangement of plagioclase, orthoclase, muscovite, biotite, and quartz. The average composition of the xenolith is similar to that of a potash-rich granite (see analyses below, and compare with the analysis of Shap

granite). The potash-soda-lime ratio, calculated as felspar, is approximately $Or_{54}Ab_{40}An_6$.

	(*a*)	(*b*)
SiO_2	64·80	67·03
TiO_2	—	0·63
Al_2O_3	19·87	16·66
Fe_2O_3	0·25	0·48
FeO	—	3·96
MnO	—	0·27
MgO	0·26	1·84
CaO	0·48	0·70
Na_2O	3·04	2·59
K_2O	10·96	5·13
$H_2O+110°$ C.	—	0·49
$H_2O-110°$ C.	—	0·11
CO_2	—	nil
Loss	0·70	—
Total	100·36	99·89

(*a*) Orthoclase porphyroblast from xenolith of Malmesbury shale in Kloof granite, Cape Town, South Africa. $Or_{64·79}Ab_{25·69}An_{2·40}$.

(*b*) Banded xenolith of Malmesbury shale in Kloof granite, Cape Town, South Africa.

It is interesting to observe that if the metamorphism of this particular xenolith had been carried to the stage of complete holocrystalline reconstitution, with homogenization of the felspar porphyroblasts, but without actual fusion, the result would have been a rock closely resembling—if not identical with—a porphyritic potash-rich granite. The possibility that such rocks may be derived by metamorphism, well below the solidifying temperatures of igneous rocks, indicates the difficulties of the problem, and the need for caution in the use of crystallization diagrams where there is not convincing field evidence of the magmatic origin of the rock in question.

IX. Summary.

The common occurrence of the microcline form of potash-soda-felspar in pegmatites may be due to the crystallization temperature of the latter falling within the perthite exsolution range. At these relatively low temperatures the oblateness of the indicatrix is a maximum, and this, together with the fact that exsolution and crystallization of the two felspars are taking place simultaneously, provides the optimum conditions for the formation of microcline. The parallel orientation of the albite and the microcline twinning in coarsely perthitic microcline supports this view.

The derivation of the common potash-rich pegmatites from granite magmas cannot be satisfactorily explained by the existing binary or ternary crystallization diagrams. To overcome the various difficulties, the writer suggests that the residual granite magma has separated into two fractions, one rich in potash, which produced the ordinary pegmatites, the other rich in soda, which produces the complex pegmatites, and possibly much of the myrmekite of granites. This suggestion involves a modification of the binary diagram for temperatures below 750–800° C., and accounts for the following facts:

1. The potash-rich character of the ordinary pegmatites, and their preponderance over the complex albite-rich pegmatites.

2. The final graphic cotectic of quartz and microcline, or alternatively, of quartz and oligoclase.

3. The absence of the ternary graphic cotectic of quartz, microcline, and plagioclase from these low-temperature crystallizations.

4. The quartz-oligoclase cotectic composition of the myrmekite of granites, on the assumption that some part of the albite-rich immiscible magma has been retained in the crystal mush.

5. A last-stage albite-rich magma which gave rise to the complex pegmatites.

This view of two immiscible magmas derived from a common granite magma has been put forward by other workers to explain special field problems.

Microperthitic exsolution causes an increase in density. Very high pressure would tend to promote exsolution and so modify the exsolution curve, and indirectly, the binary cotectic crystallization diagram, by increasing the immiscibility gap. Potash-soda-felspars which have crystallized from granitic magmas under very high pressures should thus tend to have a lower soda-content than the normal, and show the orthoclase rather than the microcline form.

The occurrence of potash-soda porphyroblasts in xenoliths and similar metamorphosed rocks under conditions which preclude an origin by direct crystallization from a magma, raises the question as to how far it is justifiable to regard holocrystalline rocks, even of typical granitic appearance, as products of direct magmatic crystallization. The same process which gave rise to these porphyroblasts, if continued for longer periods or at elevated temperatures, might produce holocrystalline granitic rock structures without the mass having even approached the liquid state.

For such rocks the ordinary solidus-liquidus diagram would have no

meaning, but even under these conditions, crystallization of the potash-soda-felspars would still conform to the exsolution curve, whose immiscibility gap would depend on the particular formation temperature. A consideration of the composition and degree of heterogeneity of the contained potash-soda-felspars might provide useful information about the temperature and condition of formation.

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Correction to Part I (Min. Mag., 1937, vol. 24), p. 472, lines 2–3 from bottom: delete 'the results are set out in the lower curve of Fig. 18'.

On the nature of withamite from Glen Coe, Scotland.

(With Plate IV.)

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[Read March 10, 1938.]

IN 1824 Henry Witham discovered a beautiful red epidote mineral in the lavas of Glen Coe, Argyllshire, which was described by Brewster[1] nder the name withamite. An analysis was made by Coverdale[2] of bviously highly impure material, but later a more complete one was rried out by Heddle[3] on carefully hand-picked mineral. Heddle[4] dmits, however, that his analysis shows 'by no means a satisfactory greement with the composition of epidote', and from his figures it ould seem very likely that his analysed material was also impure. In e Glen Coe Geological Survey Memoir[5] no further data were recorded of is mineral, Heddle's analysis and description merely being quoted.

The writer visited Glen Coe and collected material in a cutting on the ew road, approximately 5½ miles west of King's House (Geological rvey, sheet 53), where it is fairly well exposed. It occurs in a fine-rained, rather altered andesitic rock, as narrow veinlets up to 120 mm. length and 50 mm. in width; also as infillings of vesicles. The veinlets ay be straight or highly irregular; in the former case they possibly llow joint-planes, for the rock will often fracture along such a plane, roducing one or two surfaces covered with the red epidote mineral. he vesicles vary greatly in size from approximately 0·3 to 70 mm., and the larger ones calcite is a common associate. Whether in vein or

[1] D. Brewster, Description of withamite, a new mineral species found in Glenco. dinburgh Journ. Sci., 1825, vol. 2, pp. 218–221.

[2] T. Thomson, Outlines of mineralogy, geology and mineral analysis. London, 36, vol. 1, p. 377.

[3] M. F. Heddle, Minerals new to Britain. Min. Mag., 1882, vol. 5, pp. 1–25 ithamite, p. 15).

[4] M. F. Heddle, Chapters on the mineralogy of Scotland. Trans. Roy. Soc. inburgh, 1899, vol. 39, p. 355.

[5] E. B. Bailey and H. B. Maufe, The geology of Ben Nevis and Glen Coe. Mem. ol. Surv. Scotland, (sheet 53), 1916, p. 179.

vesicle, this epidote mineral always appears to be separated from the surrounding rock by a thin layer of milky-white epidote. Some of the vesicles may also be filled with a deep-green epidote. Rarely it occurs in a fine-grained reddish-brown andesitic rock which appears to be a phase of the main rock type, the colour being due to brownish-red oxides of iron.

In thin section the vesicles average about 1·0 mm. across. The epidote mineral which entirely fills the vesicles may be: (1) a single grain often with subidiomorphic to idiomorphic outline; or (2) much more frequently a mass of radiating fibres diverging from one or more centres. This radiate or spherulitic arrangement is often so well developed (pl. iv, fig. 5) that a perfect black cross may be seen between crossed nicols. In the reddish-brown rock, the vesicles may contain some xenomorphic quartz.

The chemical composition of the epidote mineral varies between wide limits in separate vesicles and even in the same vesicle. The variation is particularly well shown where radiating fibres are developed; in this case the centre or nucleus of the 'spherulite' is usually a dark red, while the outer extremities of the fibres are common, pale yellow, moderately ferruginous epidote. From the centre to the extremities there is a complete and gradual variation in the colour (pl. iv, fig. 5). Rarely in the larger amygdales, instead of a gradual change in colour, there may be a rather sharp zonary banding. In one beautiful example (pl. iv, fig. 3) of radiate arrangement from three centres, besides the usual gradual change in colour, there are three zonary bands, the widest 0·2 mm. in width, in which the epidote mineral appears to be filled with tiny inclusions. Such radiate arrangement with red centres grading off into colourless borders is not an unusual feature in piedmontite, similar occurrences having been noted by Lausen[1] from Pat Hills, Arizona, by Guild[2] from Tucson Mountains in the same state, and by Yamasaki[3] from Shinano, Japan. Chemically, this colour variation is due to the gradual decrease in the Mn_2O_3 content outwards from the centre, the latter giving strong reactions for manganese, while the pale yellow or colourless epidote shows only a trace.

With the object of discovering the exact chemical composition of the

[1] C. Lausen, Piedmontite from the Sulphur Spring Valley, Arizona. Amer. Min., 1927, vol. 12, pp. 283–287. [Min. Abstr. 3–456.]

[2] F. N. Guild, Piedmontite in Arizona. Amer. Min., 1935, vol. 20, pp. 679–692. [M.A. 6–380.]

[3] N. Yamasaki, On the piedmontite-rhyolite from Shinano. Neues Jahrbuch Min., 1898, vol. 2, pp. 253–254.

ed epidote, the mineral was separated from a specimen in the museum f the Department of Mineralogy and Petrology, Cambridge. By careful anipulation, finally in Clerici solution, it was possible to free the con-ntrate from all the colourless epidote. The analysis of this is given nder B in table I. Material collected on a visit to the locality made possible to obtain a greater quantity of concentrate by ordinary paration methods. This concentrate was ground down to pass through 300-mesh sieve and then centrifuged so that a more dense, i.e. more anganiferous concentrate than that analysed before was obtained nalysis C). It must be pointed out, however, that these two analyses, ough of a perfectly pure epidote mineral, represent the concentrate hich optically does show slight variation, especially B. Nevertheless ey serve to show the nature of the red epidote mineral.

TABLE I. Analyses of withamite from Glen Coe.
(A by M. F. Heddle, 1882; B and C by C. O. Hutton.)

	A.	B.	C.
SiO_2	43·230	38·75	37·57
Al_2O_3	23·090	24·71	24·70
Fe_2O_3	6·675	10·77	11·31
TiO_2	—	0·41	0·24
FeO	1·131	n.d.*	n.d.*
MgO	0·884	0·43	0·09
Mn_2O_3	0·138 (MnO)	0·83	0·96
CaO	20·003	21·86	23·32
SrO	—	0·31	0·09
Na_2O	0·935	0·26	nil
K_2O	0·962	0·11	nil
Li_2O	0·253	n.d.	n.d.
$H_2O+110°$ }	2·400	1·93	1·83
$H_2O-110°$ }		0·07	0·21
	99·701	100·44	100·32
Sp. gr.	—	3·38–3·40	3·39–3·40

* Owing to the presence of Mn_2O_3 in the mineral, FeO cannot be determined with y approach to accuracy.

Although the structure of epidote is not yet fully understood, the nalyses B and C have been calculated in table II on the basis of 13 xygen atoms to the unit cell and the results expressed by the structural rmula suggested by Machatschki,[1] viz. $X_2Y_3Z_3$ $(O,OH,F)_{13}$.

Machatschki states that manganese may come in to either the X or ie Y groups or be spread between them by reason of the intermediate

[1] F. Machatschki, Die kristallochemischen Beziehungen zwischen Epidot-Zoisit nd Orthit-Allanit. Centr. Min., Abt. A, 1930, pp. 89–96. [M.A. 4–357.]

TABLE II. Calculation of chemical formulae.

	B.	Metal atoms.		C.	Metal atoms		
SiO_2	38·75	3·046	3·04z	37·57	2·979		3·00 z
Al_2O_3	24·71	2·284		24·70	2·304	0·021	
						2·283	
Fe_2O_3	10·77	0·623	2·99 Y	11·31	0·675		3·00 Y
TiO_2	0·41	0·023		0·24	0·014		
MgO	0·43	0·052		0·09	—		
Mn_2O_3	0·83	0·046		0·96	0·057	0·028	
						0·029	2·01 X
CaO	21·86	1·842	1·90 X	23·32	1·984		
SrO	0·31	0·014		0·09	—		
Na_2O	0·26	—		nil	—		
K_2O	0·11	—		nil	—		
$H_2O+110°$ ...	1·93	1·010	1·01	1·83	0·951	0·95	
$H_2O-110°$ ...	0·07	—		0·21	—		
	100·44			100·32			

B gives the formula (OH) $(Ca,Sr,Mn)_{1·9}$ $(Al,Fe,Ti,Mg)_{2·9}Si_3O_{12}$.
C „ „ (OH) $(Ca,Sr,Mn)_2$ $(Al,Fe,Ti,Mn)_3$ $(Si,Al)_3O_{12}$.

ionic radius of that cation. In B all the manganese is required in the X group, while in C it is divided between groups X and Y in the ratio 0·029:0·028. The aluminium cation does not enter the four-co-ordinated group z in B, but does so in C to the slight extent of 0·021. (OH) in C is very slightly short of the figure required by the above formula.

The determination of water was carried out according to the method of Penfield,[1] but with the use of a silica tube and the oxy-coal gas blow-pipe flame, for the heat of the Meker burner is not sufficient to drive off all the (OH) as Smethurst[2] found when analysing epidotes from the Malvern Hills. Even his fusion with sodium tungstate at 1000° C. failed to liberate the amount of water demanded by the structural formula. Although the present writer found that the Glen Coe mineral failed to yield its total water on fusion with Na_2WO_4, it readily did so before the blowpipe. Smethurst, however, does not appear to have employed the latter method of attack.

The optical characters of the material (analysis C) for sodium-light are

α 1·733, β 1·750, γ 1·762,[3] all $\pm$0·002; $\gamma-\alpha$ 0·029.

Elongation β, $a:c = +2°\pm1°$; 2V 78°$\pm$1°, negative.

α clear yellow, β pale amethyst, γ deep purplish red; $\gamma>\alpha>\beta$.

[1] W. F. Hillebrand and G. E. F. Lundell, Applied inorganic analysis. New York 1929.

[2] A. F. Smethurst, Anomalies in the analytical determination of water in epidote. Min. Mag., 1935, vol. 24, pp. 173–179.

[3] A few grains gave a γ value as high as 1·767$\pm$0·002.

From the analyses and the optical data it would seem reasonable to consider the red mineral a poorly manganiferous piedmontite. The three refractive indices of the mineral are slightly higher than that of a common epidote having a Fe_2O_3 content of 11–12 %; these would be:

Epidote.[1]	Glen Coe mineral.
α 1·730	α 1·733
β 1·749	β 1·750
γ 1·760	γ 1·762

This increase is most probably due to the incoming of approximately 4–5 % of the $(OH)Ca_2(Al,Mn)_3Si_3O_{12}$ molecule. If it had been possible to obtain a concentrate of the most deeply coloured mineral, which unfortunately always occurs at the centre of the smaller amygdales, it is probable that the Mn_2O_3 content would have approached a figure in the neighbourhood of 2 %.

The characteristic feature of the pleochroic scheme of the Glen Coe mineral is the pale tint for the β vibration-direction, a feature in which it strongly resembles piedmontite from western Otago, New Zealand;[2] although the absorption of the latter mineral is much more intense. Lacroix,[3] though he does not state the absorption, compares the pleochroism of the Glen Coe mineral with that of piedmontite from Saint Marcel in Piedmont and Jakobsberg in Sweden.

The association of piedmontite with lavas is frequently the case in American localities where the mineral has been observed in rhyolites,[4] andesites,[5] and felsites.[6] For the source of the various components necessary for the formation of this poorly manganiferous piedmontite the writer does not believe that it is necessary to look beyond the lavas themselves, for the break-down of ferromagnesian minerals and felspars would supply all the necessary oxides including manganese. This supposition does not necessarily assume that the ferromagnesian constituents were rich in manganese, for the piedmontite merely represents a concentration of the manganese which was probably derived from a large

[1] A. N. Winchell, Elements of optical mineralogy. New York, 1933, pt. 2, p. 313.

[2] F. J. Turner, Note on the occurrence of piedmontite in quartz-muscovite-schist from Shotover valley, western Otago, New Zealand. Min. Mag., 1933, vol. 23, pp. 416–418.

[3] A. Lacroix, Propriétés optiques de la withamite. Bull. Soc. Franç. Min., 1886, vol. 9, pp. 75–77. Matériaux pour la minéralogie de la France. IV. Épidote manganésifère (piédmontite) de l'île de Groix. Ibid., 1888, vol. 11, pp. 148–149.

[4] G. H. Williams, Piedmontite and scheelite from the ancient rhyolites of South Mountain, Pennsylvania. Amer. Journ. Sci., 1893, ser. 3, vol. 46, pp. 50–57.

[5] C. Lausen, loc. cit.

[6] F. N. Guild, loc. cit.

volume of andesite. In the piedmontite-bearing felsites from Tucson Mountains, Arizona, Guild (loc. cit., p. 691) shows that the manganese content is no more than is frequently found in normal rhyolitic rocks, and hence states that 'a rock, in order to develop piedmontite does not necessarily have to contain more manganese than is found in normal rocks'. A glance at the analyses of the Glen Coe rocks in the Geological Survey Memoir (loc. cit., pp. 182–183) does not show one with any abnormal amount of manganese. Whatever physico-chemical conditions are necessary for the formation of piedmontite rather than normal epidote, it is clear that those conditions did not obtain for the entire period required for the infilling of the cavities and veinlets, but that they gradually changed. Thus on the outer borders of the amygdales we have not piedmontite but a common epidote with an iron content[1] identical or very close to that of the piedmontite in the centre.

There is no evidence what these physico-chemical conditions were, but two possible hypotheses may be suggested:

(1) Temperature of the circulating solutions may have played some part, a higher temperature facilitating the formation of the piedmontite molecule. With a gradual decrease in the value of this factor, conditions favourable for the production of a manganiferous epidote slowly failed, a normal epidote forming instead. (2) There may have been merely a gradual failure in the supply of manganese.

Acknowledgements: The writer wishes to express his gratitude to Professor C. E. Tilley for his advice and constructive criticism. To Mr. Arthur Russell of Reading and Dr. A. M. Cockburn of Edinburgh, I express my indebtedness for their kindly assistance with material.

Explanation of Plate IV.

Withamite from Glen Coe, Scotland.

Fig. 1. A polished specimen of a large amygdale (broken in two), showing much withamite, the milky-white outer zone of epidote and plentiful calcite. ×¾.

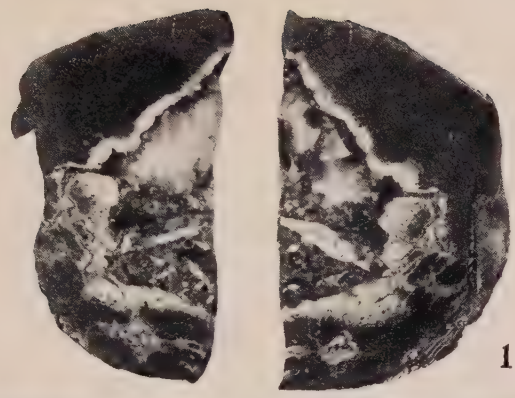
Fig. 2. An irregular amygdale showing radiating structure with dark red centre or nucleus, in fine-grained andesitic rock. ×30.

Fig. 3. A large amygdale with the withamite radiating from three centres and also a zonary banding of dark inclusions. ×30.

Fig. 4. Amygdale showing subidiomorphic to idiomorphic outline of withamite with slight radiate arrangement, and fairly plentiful quartz. ×30.

Fig. 5. An amygdale with perfect spherulitic arrangement and deep red, manganese-rich centre. ×30.

[1] Fe_2O_3 content was estimated by means of an approximate determination of the birefringence with a quartz wedge.



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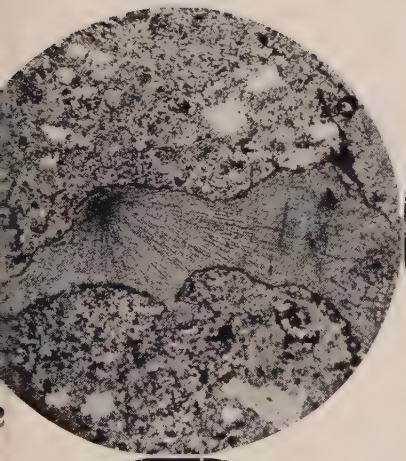

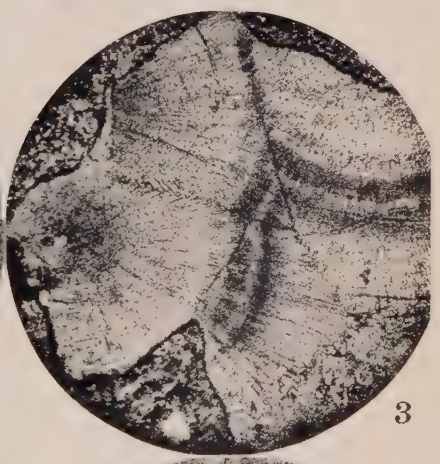

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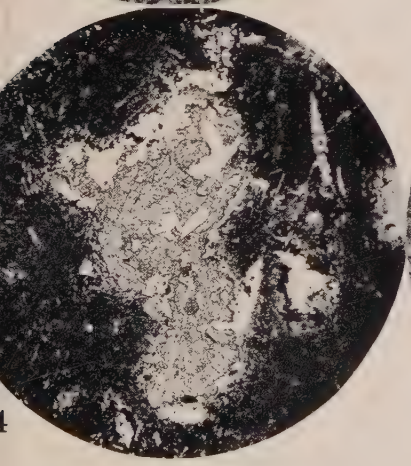

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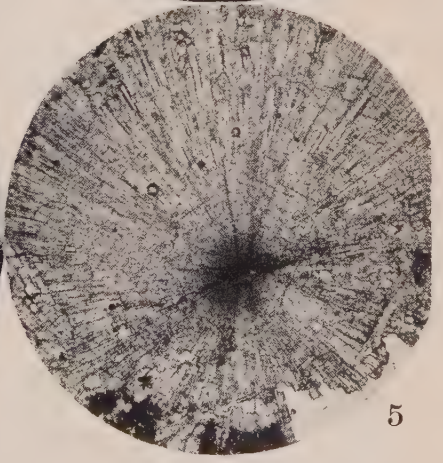

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C. O. Hutton: Withamite from Glen Coe.

Tabular spessartine crystals in muscovite.

By Edgar D. Mountain, M.A.
Professor of Geology, Rhodes University College, Grahamstown,
and Leslie E. Kent.[1]

[Read March 10, 1938.]

DURING the course of a survey of the mineral deposits of the area immediately south of the Murchison Range in the NE. Transvaal, a visit was paid to the Union mica mine, one of the only two producing mica mines in South Africa. Interest very soon centred round the occurrence of flattened garnet inclusions in a large number of the mica sheets inspected in the trimming hut. A description has been given by A. L. Hall[2] of the nature of the occurrence of the muscovite, while the geology of the area surrounding the mine is shown in a general way on his map. However, no mention was made of platy garnet crystals; and the Union mine is shown on the map as the Premier mica mines, a name by which it was then known. It is situated on the farm Inyoko (or Inyoka) (24° 8′ 25″ S., 30° 50′ 49″ E.) on the western slopes of a ridge overlooking the Sandspruit valley, and lies only two miles from Mica Siding on the Selati Railway, though best approached from Gravelotte by road, a distance about 22 miles.

The mica, which occurs as large books in coarse pegmatite injecting the Old Granite, is won by means of a complicated system of tunnels, winzes, drives, and chambers, and in fact the mine has followed the sporadic occurrence of books and shoots of muscovite down to 160 feet. When seen by the fitful light of a torch reflected from the myriad glistening sheets of mica studding the walls and lying as fine waste on the floor, these chambers seem veritable Aladdin's caves. It is noticeable that the larger books of mica are invariably associated with the more felspathic pegmatites.

The pegmatites consist essentially of quartz and white felspar usually segregated into patches several inches or even feet across and rarely in graphic intergrowth. The most extraordinary feature is that all the

[1] With permission of the Hon. the Minister of Mines, Union of South Africa.
[2] A. L. Hall, Mica in the eastern Transvaal. Mem. Geol. Survey, South Africa, 1920, no. 13. [Min. Abstr. 1–270.]

felspar appears to be albite. Some of it certainly does not show albite twinning under the microscope in thin sections, but every sample crushed for examination revealed a certain amount of fine polysynthetic twinning and the optical properties agree with albite containing only a few per cent. of the anorthite molecule. This albite occurs as cleaved masses up to several inches across showing well-defined twinning macroscopically, but also in sub-parallel aggregates and somewhat radiating masses of presumed later origin. While it seems reasonable to regard this latter as of secondary origin, however, it is difficult to see how the large individuals can be regarded as anything but primary. The more intimate associations fail to give any definite clue as to replacement, but it should be noted that no microcline or orthoclase was actually observed which might have represented original unreplaced felspar. The identity of the felspar as albite was established by A. L. Hall by chemical analysis, but he does not appear to have stressed the peculiar fact that microcline, the common felspar of pegmatites, is either absent or very subordinate.

Other minerals which are common in the pegmatites and occur in the specimens examined are muscovite and garnet, while apatite occurs but rarely. Muscovite is common throughout the pegmatites and is usually of a greenish or more rarely brownish tint. Rough tests gave the following figures: sp. gr. 2·9, β 1·595, 2V 40°, which are characteristic of ordinary muscovite, so that no further work was done on it. The garnet crystals are described separately, and the only other mineral was a pale blue apatite. This from its refractive index is fluor-apatite, and occurs as columnar masses enclosing quartz and apparently replacing albite. It is of interest that A. L. Hall mentions apatite enclosed in garnet.

The garnet occurs in two fairly distinct ways which may be conveniently referred to as rounded and flattened respectively. The rounded type occurs only at the margin of the mica books. That portion or those specimens which occur just within the mica are invariably idiomorphic crystals up to 2 cm. diameter consisting of the icositetrahedron modified by the rhombic-dodecahedron; while those just outside the mica and thus within the pegmatite are generally in the form of irregular masses, sometimes weighing several pounds and completely lacking in crystal facets. These rounded forms are usually of a deep reddish-brown colour and practically opaque in the hand-specimen except for the smaller idiomorphic specimens. They are, moreover, largely altered to a limonitic product. Tested chemically they are found to contain a high percentage of manganese.

The flattened garnets, on the other hand, occur exclusively within the ica books, the plane of flattening being invariably parallel to the leavage-plane of the mica. They appear to be limited in their distribu- ion to certain layers within the mica and are more prevalent towards he outer fringes of the books. In addition, they are more frequently ncountered in the larger books. In thickness they vary from 0·1 to 5 mm., being on the average 1–2 mm., while in diameter they range rom that of a pin's head up to 2 cm. The flattest garnet encountered as 12 mm. in diameter and only 0·25 mm. in thickness. According to Ir. F. Burch, a former manager of the mine, they are thicker on the verage in the 'edge-waste' of the books than within the larger leaves. hey vary in colour from a pale brownish-pink to a deep ruby-red.

These flattened garnets occur sometimes as isolated crystals and some- mes in strings, in which case they tend to be nearer to the outer margin f the books. Such strings of garnet (figs. 1 and 3) consist usually of ny crystals up to 2 mm. across and 0·3 mm. in thickness. They are ound in a feathery type of muscovite in which the large plates are ivided up into areas, each characterized by a sort of fluting or foliation arallel to the rays of the pressure-figure of the mica respectively. Now ach of these foliated areas contains only strings of garnet crystals erpendicular to this foliation, and thus the strings are arranged parallel the traces of the unit prism and clinopinakoid, or, in other words, arallel to the rays of the percussion-figure (fig. 4). The strings are paced irregularly, and parallel to them are also other lines of distur- ance without the presence of garnets. Within the strings the tiny rystals are themselves spaced at irregular intervals, but generally the rger the crystals the greater the space between them. Occasionally ich strings penetrate a considerable thickness of the mica book, the arnets then lying in a plane roughly perpendicular to the mica cleavage.

Thirty crystals, both of the isolated type and of those in the strings, ere detached and examined carefully on the two-circle goniometer, eing mounted on the large face; but before removal the trace of the ptic axial plane of the muscovite was ruled on one of the large faces f each crystal. They sometimes possess a fairly regular six-sided out- ne (fig. 2) and may be distinctly elongated parallel to a pair of these dges, but generally possess a somewhat rounded or polygonal outline. hey also occur in parallel growths and in groups of two or three irregu- rly associated. The large face rarely gives a good image owing to ppreciable convexity, and it frequently carries a pattern of growth-pits hich, however, proved useless for orientation purposes. The edges of

the tablet are usually modified by half a dozen or so recognizable faces, but the rest of the margin is usually indistinct and fluted. In spite of this, however, a number of reflections were obtained on the goniometer from ill-defined faces. These showed that the crystals are nearly always tabular near a face of the rhombic-dodecahedron and that other reflec-

FIG. 1. FIG. 2.

FIG. 1. Rows of garnet crystals in muscovite arranged perpendicular to fluting. $\times \frac{1}{2}$.

FIG. 2. Typical garnet crystals enclosed in muscovite. $\times 3$.

tions all belong to either the rhombic-dodecahedron or the icositetrahedron (211). Faces of the former usually give the better reflections, while the latter tend to be striated parallel to their intersection with the former.

Where a dodecahedral face is located at anything over $\rho = 5°$ or so, it appears distinctly as a sort of vicinal face modifying the large face and recognizable in the hand-specimen. In this case the large face gives a number of images, both isolated and in strings, and of varying degrees of definition within a radius of 5°, corresponding to various vicinal faces

and zones of faces. In those cases where the pole of the plane of flattening departs appreciably from that of a dodecahedral face it is found to lie roughly on one of the principal zones passing through a dodecahedral face, but in only one case did it lie between the dodecahedron and cube. The poles were plotted on a gnomonic projection on a (110) plane as shown in the diagram (fig. 5), only those falling outside the 3° radius

Fig. 3.

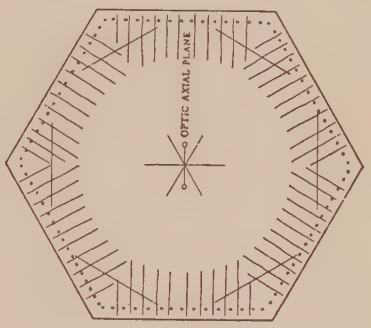

Fig. 4.

Fig. 3. Rows of garnet crystals in muscovite arranged perpendicular to fluting. Straight lines are planes of parting. Sketch of the plate, a portion of which is shown in fig. 1.

Fig. 4. Diagram to illustrate the orientation of rows of garnet crystals with respect to the fluting, planes of parting, percussion-figure, and optic axial plane of the muscovite.

being indicated; 18 poles out of the 30 thus fell within 3° of a dodecahedral face. It will be noticed that flattening does not occur anywhere near a cubic face.

With regard to the orientation of the garnet individuals relative to the trace of the optic axial plane of the muscovite, very little can be stated. There is, however, a strong tendency for the optic axial plane to lie parallel to either the longer or the shorter diagonals of the dodecahedral face on which flattening occurs, while other cases occur where it lies definitely parallel or perpendicular to a side of the face. The results of the goniometric measurements show conclusively that there is no common orientation.

A few of the thicker crystals possess marked parting-planes parallel

to faces of the rhombic-dodecahedron, especially developed parallel to the large face of flattening. The specific gravity determined in Clerici solution was found to vary slightly, being about 4·10. The pale brown crystals have a slightly lower figure than the deeper-coloured ones. Under the microscope, the crystals are mostly quite isotropic and their refractive index is about 1·805–1·810, but no variation was observed. A few of the crystals show well-defined colour zoning, the inner zones being polygonal but not necessarily of the same shape as the crystal outline.

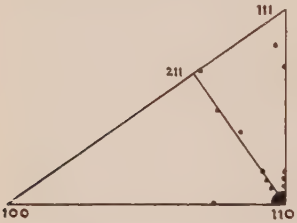

Fig. 5. Gnomonic projection showing orientations of the plane of flattening of 30 garnet crystals. The large dot around (110) represents 18 of them.

A clear reddish tabular crystal weighing 0·3 gram was crushed and a rough analysis was made of the iron and manganese. The iron was determined by titration with titanous chloride and the manganese colorimetrically after oxidation with sodium bismuthate, giving total iron (as FeO) 16 % and MnO 24 %, which correspond to $Alm_{40}Sp_{60}$. A number of other crystals were tested with the sodium carbonate bead and found to be rich in manganese, so that all the garnets are assumed to consist predominantly of the spessartine molecule.

The garnet crystals are in general not situated on the surface of the muscovite books but are very definitely enclosed deep within them. They have, however, influenced the adjacent cleavage-layers and leave a slight hollow where the immediate layers have been in contact with the crystals, an effect which is noticed through a different thickness of mica in different cases. The mica layers in a continuous plane with the crystal tablet stop abruptly against the edge of the tablet usually without modification except for the existence of a system of radial cracks in the mica presumably due to pressure, like expansion cracks commonly found round olivine crystals altered to serpentine. The pressure exerted by the garnet on the surrounding muscovite is not regarded necessarily as an effect of the original crystallization of the garnet, but may possibly be due to subsequent alteration of the garnet crystals caused through oxidation of ferrous iron. The garnet crystals themselves, especially the larger ones, are commonly riddled with cracks as though they had been under strain.

In 'Ore deposits of the Western States' (p. 144 et seq.),[1] W. T. Schaller

[1] Amer. Inst. Mining and Metall. Engineers, Lindgren volume, 1933. [M.A. 6–3.]

states that irrespective of whether the original pyrogenic rock of the pegmatites consisted essentially of potash-felspar or of graphic granite or both, the outstanding fact of pegmatitic development is that the aggregates of albite, micas, garnets, and many other minerals are formed by later hydrothermal replacement processes acting on and replacing the first formed potash-felspar rock. As stated previously, it would appear that the parent rock in the present case was essentially albite-quartz-pegmatite, though some of the albite is almost certainly secondary. Of the other minerals, Schaller gives the following order: albite, muscovite, and the general group including tourmaline, garnet, and beryl. Where the garnet occurs in the albite or micropegmatite, the appearance of the garnet and its mode of occurrence suggest that it was formed at the expense of the felspar, but where the garnet occurs in muscovite, the case for replacement and a later age for the garnet is not so clear. It is difficult to imagine, perhaps, some of the larger garnets up to 2 cm. across developing in a book of muscovite by replacement, but such a process may nevertheless be possible.

The principal features of the garnet are the habit of the flattened crystals and the arrangement in strings. In Dana's 'System of Mineralogy' (6th ed., 1892, p. 619) appears the following statement: 'Muscovite often encloses flattened crystals of garnet, tourmaline, also quartz in thin plates between the sheets; further, not infrequently magnetite in dendrite-like forms following in part the directions of the percussion figure, also those of the pressure figure.' It might be added that white chalcedony occurs in films up to 8 mm. thick, interleaved with the mica now described, and is associated with films and even small crystals of quartz. The thicker films consist sometimes of alternating bands of dull white chalcedony and clear quartz and resemble extremely flattened agates in structure. These, however, appear to be almost entirely confined to the upper 40 feet of the workings and are therefore limited to the zone of oxidation. They show that on weathering the muscovite has become invaded by siliceous solutions.

Even under stress conditions garnet crystals usually have an equidimensional development, thrusting aside other minerals by their power of crystallization in such rocks as garnetiferous mica-schist, and consequently there seems to be no doubt that the tabular habit is due not to mechanical forces, but to some influence of the muscovite on the molecular aggregation of the garnet crystals. Dr. R. Brauns in his book 'The Mineral Kingdom'[1] writes: 'Enclosures of other minerals in musco-

[1] English translation by L. J. Spencer, 1912, p. 331.

vite are frequent and are of special interest. Growing along with the mica between its planes of lamination these foreign minerals have been constrained to take a thin, flattened form. Thus crystals of garnet, which are so characteristically rounded or grain-like in form, when found embedded in sheets of mica have the form of thin plates with an almost circular outline. . . . That mica is capable of exerting some influence over the crystallization of other substances is shown by the following simple experiment. An aqueous solution of potassium iodide when allowed to crystallize on a glass plate produces a crop of thick cubes. If, on the other hand, the solution is crystallized on a clean, fresh cleavage sheet of mica, the crystals of potassium iodide take the form of flattened octahedra; and not only this, but the tiny crystals are all regularly oriented in the same direction on the sheet of mica, one of their triangular edges being parallel to the optic axial plane of the mica.' From these considerations it seems certain that in our case the muscovite is not merely moulded on earlier formed garnet crystals, but that already crystallized muscovite has influenced the habit of the garnets. This, of course, will explain why the flattened crystals are found within the mica books, while the rounded type is found only at the margin where the crystal structure of the muscovite has had no influence on their habit.

In two recent papers in the 'American Mineralogist'[1] there are described oriented inclusions of tourmaline, magnetite, and haematite in muscovite; and the authors incidentally referred to flattened garnet crystals, though without any details. In the case of magnetite the flattening is perpendicular to a threefold axis, and the authors showed that a close similarity exists between the spacing of the oxygen atoms parallel to the basal plane of muscovite and those of an octahedral plane of magnetite. In the case of garnet the crystals are flattened parallel to a rhombic-dodecahedral face and not an octahedral face. From data kindly supplied by the Royal Institution, the arrangement of the oxygen atoms in this plane has been plotted, but no appreciable amount of coincidence with those of the basal plane of muscovite could be recognized. The silicon atoms were also plotted, in both cases with similar negative results. In the cases mentioned here, where the trace of the optic axial plane of the muscovite is parallel to one of the diagonals of the dodecahedral face of flattening of the garnet, the plane of symmetry of the muscovite corresponds to a plane of symmetry of the

[1] C. Frondel, 1936, vol. 21, p. 777; C. Frondel and G. E. Ashby, 1937, vol. 22, p. 104. [M.A. 6–517, 518.]

arnet, but apart from these two directions at right angles there are o other coincidences among planes of low indices.

The existence of strings of garnets in lines parallel to what would resumably during growth be the equatorial faces of a crystal of musco-ite suggests further that they have developed along growth-planes, and nus simultaneously with the muscovite. On the other hand, growth-lanes are likely to be, and definitely are, planes of weakness, and it is ossible that hydrothermal solutions could have followed such lines and ntroduced the material of the garnets subsequently.

Evidence has already been given to show that the development of arnet within the muscovite led to strains being developed in the mica, ut the layers of muscovite are far from being entirely bent round the nclusions 'augen'-fashion. In fact, the muscovite appears to be only ightly disturbed in contact with the edges of the garnet tablets. Small nomb-shaped highly birefringent strips of muscovite sometimes occur ithin the books near the garnet crystals and at first it was thought that ey were fractured pieces which had been introduced subsequently, but one or two cases these fragments were embedded in a ferruginous atrix.

In two cases of very flat crystals there is a narrow green zone along art of the margin of what appeared to be the garnet crystal, while the rrounding muscovite was also a little deeper green than the rest. This een marginal zone in the garnet was found to be soft and when the owder was examined under the microscope it was seen to consist of assive mica with an optic axial angle somewhat smaller than the rdinary muscovite, but similar in other respects and showing aggregate olarization. The garnet portion consists of a parallel growth of crystals assing into isolated crystals in the green marginal matrix, themselves ranged in parallel positions. This kind of crystalline habit does not em to support any suggestion that garnet crystals have been produced replacement within the large muscovite plates. Moreover, the occur-nce of euhedral zoned garnet crystals within the muscovite is surely ot reconcilable with a replacement origin so far as replacing muscovite concerned.

In conclusion, then, garnet inclusions flattened more or less parallel to e rhombic-dodecahedron occur in muscovite books parallel to the mica eavage without any other well-defined orientation of the crystals emselves, but sometimes occurring in rows parallel to growth-planes the muscovite. The evidence indicates that the mica cannot have veloped round these garnets, and that probably the crystallization

of garnet and muscovite was more or less simultaneous, the partially crystallized mica influencing the habit of the garnet inclusion by molecular forces.

The authors are indebted to Messrs. F. Burch and T. H. Stamp of Mica for information and specimens.

Francolite from sedimentary ironstones of the Coal Measures.

By T. Deans, B.A.

With a chemical analysis by H. C. G. Vincent, M.A.

Department of Mineralogy and Petrology, University of Cambridge.

[Read June 9, 1938; communicated by Prof. C. E. Tilley, F.R.S.]

THE sedimentary iron ores of Britain all contain small amounts of phosphorus which is generally present in the colloform mineral ollophane. In a rather uncommon class of oolitic ironstones recently escribed from the Yorkshire coalfield (1), a crystalline phosphate was ound which has now been identified as francolite and forms the subject f this paper. These oolitic ironstones occur in the immediate roofs of oal seams, are of freshwater origin, and consist of ooliths of kaolinite nd isotropic clay in a groundmass of chalybite. During the later stages t their diagenesis, francolite, associated with quartz, calcite, pyrite and lende, and much kaolinite, crystallized within the ooliths (fig. 1) and the shrinkage cracks (fig. 2) of the ironstone, and sometimes replaced ne ooliths and groundmass. The francolite is present in all of the three olitic ironstone occurrences described from Yorkshire, and also in the milar rock from Derbyshire in the Geological Survey's collection of on ores. Details of these localities are given in the ironstones paper (1). he writer has also found similar francolite in an ironstone nodule from parting in the Mühlenbach coal seam of south Limburg, Netherlands. lthough not recorded, it may be expected to occur in some of the black- and ironstones and other rocks closely associated with coal seams. The llowing account is based entirely on material from Robin Hood quarry, horpe-on-the-Hill, 4 miles south of Leeds.

Physical characters.—Pseudo-hexagonal by twinning. The crystals re hexagonal plates, consisting of the basal plane and a low pyramid, vinned in six triangular sectors. Minute re-entrant angles are frequent the corners of the plates; they are too small to measure accurately, ut are close to 120°. The crystals range up to half a millimetre across, nd sometimes up to one millimetre, but the latter are usually rounded

and covered with smaller crystals. Cleavage indistinct. Fracture conchoidal. Brittle. Specific gravity 3·21. Lustre vitreous. Colourless to pale yellow-brown. Soluble in cold dilute acid.

Optical properties.—Biaxial negative, with $\alpha = c$, and the extinction-angle, γ to the hexagonal edge, showing two different values, one about 40° (fig. 3), the other about 50°. The two values frequently occur in different sectors of the same crystal. 2V, determined with the universal

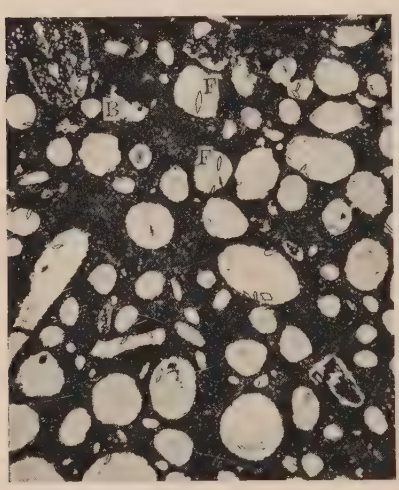

Fig. 1.

Fig. 2.

Fig. 1. Oolitic ironstone, Robin Hood quarry, near Leeds, Yorkshire. Crystals of francolite (F) and one of dark blende (B) in kaolinite ooliths. The groundmass is chalybite. Ordinary light, × 16.

Fig. 2. Shrinkage cracks in the ironstone infilled with francolite and kaolinite (fine-grained). Crossed nicols, × 16.

stage, varies from 25° at the centre of the crystal to 40° at the hexagonal edge, but the general value around the centre of the triangular sectors is about 37°. α 1·620, β 1·627, γ 1·628, $\gamma - \alpha = 0{\cdot}008$. Cross-sections of the plates indicate further twinning about a composition-plane parallel to the basal plane, but the differences in optical orientation about this plane are very slight. Many crystals show anomalous wavy extinction.

The refractive indices agree closely with previous data. In francolite from the Vosges, however, Lacroix records the optic axial plane as parallel to the hexagonal edge (2). Oblique extinctions on the hexagonal

edge occur in carbapatites and alkali-apatites. The anomalous orientation of the optic axial plane producing two extinction positions appears to be analogous to the variable orientations within the same crystal recorded in pyromorphite and endlichite by Bowman (3) and Lietz (4). The variation in the optic axial angle from the centre to the margin of the crystals is paralleled in carbapatites (5) and alkali-apatites (6) described with uniaxial cores and biaxial margins.

Chemical composition.—A mixture, almost pure, of kaolinite and francolite was scraped from septarian cracks in the ironstone. After washing to remove the finer kaolinite and crushing to pass a 400-mesh sieve, the material was centrifuged in mixtures of methylene iodide and bromoform, and the fraction with density between 3·15 and 3·21 taken for analysis. The francolite thus obtained contained inclusions of kaolinite but little other impurity. The analysis is shown in Table I.

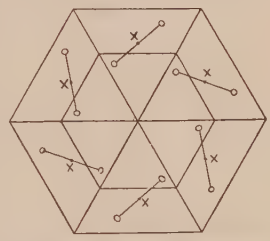

Fig. 3. Optical orientation of francolite on the basal plane.

Table I. Francolite from oolitic ironstone, Robin Hood quarry, near Leeds.

CaO	54·64	SiO_2	nil
SrO	0·13	TiO_2	nil
MgO	trace	Al_2O_3, Fe_2O_3	trace
P_2O_5	38·25	FeO	nil
CO_2	1·98	Cr_2O_3	nil
H_2O+ ...	0·66	V_2O_3, As_2O_3	nil
H_2O- ...	0·06	MnO	nil
F	2·80	BaO	nil
Insol.	2·19	Na_2O	nil
	100·71	K_2O	nil
Less O = F ...	1·18	Cl, SO_3	nil
	99·53		

In calculating the composition of the francolite the moisture and insoluble residue are ignored, and since the latter is mainly kaolinite an approximate content of 10 % H_2O+ (i.e. 0·22 %) is assumed and deducted from the combined water of the analysis, leaving 0·44 % H_2O+ for the francolite. The distribution of atoms within the molecule is calculated on the assumption that the structure is analogous to that of fluorapatite, $Ca_{10}P_6F_2O_{24}$, with 42 atoms in the molecule, and

(O,OH,F) 26. Ca, Sr, P, and C are therefore brought to a total of 16 atoms, the OH and F adjusted in the same ratio, and O obtained by difference. The composition, thus calculated, is shown in table II.

TABLE II. Atomic ratios in francolite.

	Weight %	Mol. ratios.	Atomic ratios.	Atoms to 26(O,OH,F).		Positive charges.	Negative charges.
CaO ...	54·64	9·743	Ca 9·743	9·999	10·012	19·998	
SrO ...	0·13	0·013	Sr 0·013	0·013		0·026	
P_2O_5 ...	38·25	2·695	P 5·390	5·531	5·993	27·655	
CO_2 ...	1·98	0·450	C 0·450	0·462		1·848	
H_2O+	0·44	0·244	OH 0·489	0·502	2·013		0·502
F ...	2·80	1·473	F 1·473	1·511			1·511
			O —	23·982			47·964
				42·000		49·527	49·977

The francolite may therefore be given the formula:

$$(Ca,Sr)_{10}(P,C)_6(F,OH)_2O_{24}, \text{ with the ratio } F:OH = 3:1.$$

Gruner and McConnell recently investigated a francolite (staffelite) from Staffel (7), and deduced the formula $(Ca,Mg,C)_{10}(P,V,C)_6F_2(O,OH,F)_{24}$. There is a mathematical error in their calculation, however,[1] and, corrected, the distribution of ions in the Staffel mineral is: 10Ca = 9·810Ca + 0·077Mg + 0·113C; 6P = 5·322P + 0·026V + 0·625C; 2F = 2·000F; 24O = 22·832O + 1·000OH + 0·168F. The formula for this distribution is therefore better expressed as

$$(Ca,Mg,C)_{10}(P,V,C)_6F_2OH(O,F)_{23}.$$

McConnell proposed that francolite is 'a suitable name for an apatite which contains an appreciable amount of CO_2 but which also contains more than one per cent of fluorine. It may or may not contain OH-ions' (8, p. 9). The Yorkshire material conforms to this definition of francolite, but differs distinctly from previously analysed specimens in its particularly low content of OH-ion, and relatively low C and F values. These differences probably account for the high density of this francolite as compared with previous data. The differences are to be expected, not only on account of the varied substitutions possible within the apatite group, but also on account of the different modes of origin of the francolites investigated. Some are from hydrothermal ore-deposits, others (including the Staffel material) from marine phosphorites, while the present occurrence is the first record from freshwater sediments.

[1] In table I, p. 210, of their paper, HO is 0·90 per cent., so the ionic ratio for OH should be 1·000, not 0·100 as given.

Hey has pointed out ((8), footnote p. 9) that the original francolite rom the Wheal Franco mine has never been analysed, so that the alidity of the name as applied to materials from other localities is lways doubtful. The name francolite is still used here, however, as it ould be premature to propose a new name which might have to be ithdrawn should the Wheal Franco mineral be analysed.

The author is indebted to Professor C. E. Tilley for laboratory acilities in the Department of Mineralogy and Petrology, Cambridge, nd for advice and criticism.

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On the atomic arrangement and variability of the members of the montmorillonite group.

(With Plate V.)

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[Read June 9, 1938.]

ACCORDING to their atomic arrangement the minerals found in clays can be divided into the two-layer and the three-layer structures (1). The members of the first group have alternating silica and alumina layers, e.g. kaolinite; the members of the second group have one alumina (or magnesium or iron) layer between two silica layers, e.g. pyrophyllite.[1] The clay minerals can also be classified into two groups according to their power to diffract X-rays. The first group gives good powder photographs with twenty to forty well-developed lines if copper or iron radiations are used, whereas the second group gives poor diagrams with only a few lines, usually under fifteen, some of which are wide and indistinct. Exposure times for the second group are about two to three times as large as those for the first group. The poor diffracting power for X-rays may be due either to a lack of regularity ('roughness') of the lattice, or to an extremely small size of the single crystallites. It is possible that both effects are active to some extent, but the lack of regularity of the lattice is probably the main reason. Neither the microscopic evidence nor sedimentation data based on Stokes's law show these minerals to have particles smaller than 10^{-6} cm., though it is possible that the optical effects such as double refraction are due to aggregation, and it is clear that the equivalent radius is an unsatisfactory measure for plate-shaped particles. Both classifications are shown on p. 141.

The crystal-structures of the minerals giving poor X-ray diagrams are largely derived by analogies and are not as well proved as the structures of the minerals which give good X-ray diagrams. There are

[1] The micas, chlorites, vermiculites, &c. can be considered as subgroups of the three-layer type.

	Formula	Good powder diagrams.	Poor powder diagrams.
wo layers ...	$Si_2O_5.Al_2(OH)_4$	Kaolinite, Dickite, Nacrite, Anauxite	Metahalloysite
hree layers ...	$Si_2O_5.Al_2(OH)_2.Si_2O_5$	Pyrophyllite	**Montmorillonite**
	$Si_2O_5.Mg_3(OH)_2.Si_2O_5$	Talc	**Magnesium-beidellite**[1]
	$Si_2O_5.Fe_2(OH)_2.Si_2O_5$	—[2]	**Nontronite**

lso other differences between the two types, apart from crystal size nd definition, some of which will be discussed later on.

The minerals of the three-layer type having poor X-ray powder iagrams, which are shown in heavy print in the above classification, re the subject of the present contribution. They contain, in the air-ry state, 20–23 % of water and show reversible lattice shrinkage and xpansion according to their water content. Pyrophyllite and talc, on ie other hand, contain about 5 % of water in the air-dry state and have o lattice shrinkage.

Six samples, including montmorillonite, nontronite, and beidellite ere investigated. Their chemical composition and refractive indices e given in table I.[3] The chemical data are taken from the literature -7). The refractive indices were determined on samples in equilibrium ith an atmosphere of 50 % relative humidity and on samples dried at 0° C., using a mixture of olive oil, cinnamon oil, and, if necessary, monobromonaphthalene as immersion liquid, as recommended by W. Correns and M. Mehmel (8). A sodium lamp was used as light urce and the highest indices observed on many grains were taken as '.[4] The difference in refractive indices between the two nontronites specially remarkable in view of their chemical similarity. They also ffered in colour, no. IV being yellower and no. V greener.

[1] The term 'magnesium-beidellite' is used in this paper to describe the 'bentonitic magnesian clay-mineral' from Hector, California, described by Foshag and Woodford (7) and used in this work as sample VI in table I.

[2] No mineral of the composition $Fe_2Si_4O_{10}(OH)_2$ has apparently been observed ving a powder diagram similar to the talc diagram with a basal spacing of 9·4 Å., d a dehydration curve showing a sudden loss of about 4·3 per cent. of water tween 450° and 550° C. Gruner (2) claims, however, that he obtained such a terial, at least as far as the X-ray evidence goes, by heating nontronite in a mb to 575° C.

[3] The numbers I to VI of this table will be used in the following to denominate minerals. My thanks are due to Prof. F. Heide for the material of I, to Dr. W. F. shag for II and III, to Dr. J. Orcel for IV and V, and to Dr. R. E. Grim for VI.

[4] The double refraction of all samples was of the order of 0·02 to 0·03 and was, parently, not affected by the water content of the sample.

TABLE I. Percentage composition and refractive indices of samples investigated.

	Montmorillonite	Beidellite		Nontronite		Magnesium-beidellite
	I.	II.	III.	IV.	V.	VI.
SiO_2	49·21	45·32	47·28	44·0	44·30	53·68
TiO_2	nil	—	—	—	0·18	—
Al_2O_3	22·61	27·84	20·27	3·6	5·37	0·60
Fe_2O_3	0·43	0·70	8·68	29·0	29·47	—
FeO	—	—	—	—	0·56	—
MnO	trace ?	—	—	—	—	—
MgO	2·13	0·16	0·70	2·1	1·74	25·34
CaO	1·95	2·76	2·75	—	1·70	0·52
Na_2O	0·45	0·10	0·97	—	—	3·00
K_2O	trace	0·12	trace	—	—	0·07
Li_2O	—	—	—	—	—	1·12
H_2O+	9·34	14·48	6·65	18·7	8·52	8·24
H_2O-	14·37	8·16	13·07		7·99	7·28
	100·49	99·64	100·37	97·4	99·83	99·85
$n\gamma$ for sample at 50 % rel. hum. ...	1·498	1·502	1·562	1·610	1·578	1·524
$n\gamma$ for sample dried at 100° C. ...	1·531	1·540	1·589	1·631	1·602	1·553

I. Montmorillonite, Unter-Rupsroth, Rhön. F. Heide, 1927 (3).
II. Beidellite, Black Jack mine, Carson district, Owyhee Co., Idaho. E. V. Shannon, 1922 (*4a*).
III. Beidellite, Beidell, Saguache Co., Colorado. E. T. Wherry, 1917 (*4b*).
IV. Nontronite, Nontron, Dordogne; also clay 1·2. P. Berthier, 1827 (5).
V. Nontronite, Behenjy, Madagascar. F. Raoult in A. Lacroix, 1922 (6).
VI. Magnesium-beidellite, Hector, San Bernardino Co., California; also Cl 0·31. W. F. Foshag, 1936 (7).

Chemical Composition and Isomorphous Replacement.

A complete isomorphous series between beidellite and nontronite with the end-members $Al_2O_3.3SiO_2.mH_2O$ and $Fe_2O_3.3SiO_2.mH_2O$ has been postulated by Larsen and Steiger (4) on chemical grounds. U. Hofmann, K. Endell, and D. Wilm (11), who first suggested a structure for montmorillonite, give the pyrophyllite formula plus water, $Al_2Si_4O_{10}(OH)_2.mH_2O$, with minor replacements, and J. W. Gruner (9) extends this for the whole group to the formula $(Fe,Al)_{2+\frac{n}{3}}Si_{4-n}(Al,Fe)_nO_{10}(OH)_2.mH_2O$, where n may vary between 0 and 1 and m between 2 and 5·5. The establishment of structural formulae of this kind has two difficulties. The first is the splitting of the analytical figures for water into hydroxyl groups and 'adsorbed' water, with the possible further complication of hydrogen ions. In micas, talc, pyrophyllite, and kaolinite, dehydration curves show well-defined breaks, and about the correct amount of water corresponding to the numbers of hydroxyl groups in the structure is

ven off, usually above 450° C. All these minerals belong to the group hich has well-developed powder photographs. The few dehydration irves for montmorillonite and nontronites which have been described id summarized by W. von Engelhardt (10) are, however, of a different iaracter. Large amounts of water are given off gradually to about 200°, ie curves then flatten and little water is released until about 350° to 50°, where a sudden release of about 2·3 % of water occurs, followed v a gradual further loss of one or two per cent. of water between 550° id 800°. One hydroxyl group per $Al_2Si_4O_{10}$ unit corresponds to 2·5 % f water, and it would therefore appear from these curves that the ructure contains only one hydroxyl group per $Al_2Si_4O_{10}$ unit, or that ie two hydroxyls, which are supposed to be present, and which would orrespond to a dehydration loss of 5 %, are held with different energy id are therefore not structurally identical. Far too few observations ave so far been made on these minerals, but unfortunately the small mples of material at my disposal were insufficient for detailed dehydra- on work. At present it appears from the available data that there is me reason to doubt the number of hydroxyl groups in the montmoril- nite formula $Al_2Si_4O_{10}(OH)_2.mH_2O$. The method developed by Long- hambon (12) for the study of dehydration curves of sepiolites and arious minerals seems to provide a useful advance in technique.

The second difficulty in establishing structural formulae concerns omorphous replacements. These replacements are known with cer- inty to occur in the muscovite structure, and it is only reasonable to ippose that they exist also in clay minerals of the three-layer type, but o what extent it is difficult to say. They are compatible with, but not rictly proved by, the X-ray evidence of powder photographs, a dis- nction which is often neglected in current literature.

The importance of isomorphous replacements in the layer lattices of ie clay minerals has been stressed by Marshall (13), Holzner (14), and thers, and similar calculations were made for the six samples listed in able I. The analytical figures are recalculated, in table II, for the single toms on the basis of a total of eleven oxygen atoms, after leaving out ie water percentage in view of the uncertainty of the number of ydroxyl groups present. This corresponds to the composition of one alf unit cell, if Hofmann's structure is taken as basis.

It can be seen from table II that the value of silicon varies be- ween 3·4 and 3·9. In order to bring it to 4 a corresponding number of luminium ions are taken, which are assumed to replace the silicon. For very aluminium ion which replaces one silicon ion one negative charge is

TABLE II. Number of atoms present for eleven oxygen atoms on recalculation of the chemical data of table I without water.

	I.	II.	III.	IV.	V.	VI.
Si	3·74	3·46	3·58	3·72	3·57	3·89
Al	2·03	2·50	1·81	0·36	0·51	0·05
Fe^{***}...	0·03	0·04	0·50	1·84	1·79	—
Fe^{**}	—	—	—	—	0·04	—
Mg	0·24	0·02	0·08	0·26	0·21	2·73
Ca	0·16	0·23	0·22	—	0·15	0·04
Ti	—	—	—	—	0·01	—
Li	—	—	—	—	—	0·33
K	—	0·01	—	—	—	0·01
Na	0·07	0·02	0·14	—	—	0·42

created on the lattice. In the case of the magnesium-beidellite, sample no. VI, there is not sufficient aluminium present to complete the silicon layers and a small amount of magnesium[1] ions is therefore taken to bring the number of silicon to 4. For every magnesium ion replacing silicon two negative charges are created. Table III shows the composition of the silica layers, and the sum of the negative charges created through the various replacements.

TABLE III. Atomic composition of the silica layers Si = 4 and negative charges produced.

	I.	II.	III.	IV.	V.	VI.
Si	3·74	3·46	3·58	3·72	3·57	3·89
Al	0·26	0·54	0·42	0·28	0·43	0·05
Mg	—	—	—	—	—	0·06
Negative charge	0·26	0·54	0·42	0·28	0·43	0·17

The next stage in the calculation is to build up the middle layer, which contains two aluminium, two iron, or three magnesium ions in the ideal case. If aluminium ions are replaced by magnesium ions, there are two possibilities. One magnesium can replace one aluminium and one new negative charge is created, or three magnesiums replace two aluminiums without change in the charge. This second case is possible because the aluminium ions fill only two-thirds of the available six-co-ordinated spaces in the structure, but, for reasons given below, we have used the first alternative in our calculation. In the case of the magnesium-beidellite, sample no. VI, lithium has been taken to complete the magnesium layer, again with a corresponding increase in the

[1] The replacement of silicon by magnesium is unlikely in view of the difference of the size of their ionic radii, but the amount of magnesium replacing silicon is very small, one ion out of 67, and there seems no better possibility to calculate the lattice.

gative charge. The composition of the middle layers and the charges ated are shown in table IV.

TABLE IV. Atomic composition of the middle layer, Al = 2, $Fe^{...}$ = 2, Mg = 3, and negative charges produced.

	I.	II.	III.	IV.	V.	VI.
... ...	1·77	1·96	1·39	0·08	0·08	—
... ...	0·03	0·04	0·50	1·84	1·79	—
... ...	—	—	—	—	0·04	—
... ...	0·20	—	0·08	0·08	0·08	2·67
... ...	—	—	0·03	—	(Ti 0·01)	—
... ...	—	—	—	—	—	0·33
gative charge	0·20	0·00	0·11	0·08	0·12	0·33

It is then found that after completing the structure a certain amount cations, mainly calcium and sodium, is left over in every case. They y be called excess cations, and are shown in table V.

TABLE V. Atomic composition of excess cations.

	I.	II.	III.	IV.	V.	VI.
... ...	0·16	0·23	0·19	—	0·15	0·04
... ...	0·07	0·02	0·14	—	—	0·42
... ...	0·04	0·02	—	0·18	0·13	—
... ...	—	0·01	—	—	—	0·01

adding up the valencies of the excess cations it is found that they lance fairly well the total sum of the negative charges produced rough the various isomorphous replacements[1] (table VI). This equivaice is believed not to be a chance result but to have a real significance.

ABLE VI. Sum of negative charges due to replacements, sum of positive charges due to excess cations, and base-exchange capacities of samples I to VI.

	I.	II.	III.	IV.	V.	VI.
gative charges on lattice	0·46	0·54	0·53	0·36	0·55	0·50
sitive charges of excess cations	0·47	0·53	0·52	0·36	0·56	0·51
change capacities ...	0·47	0·54	0·46	—	—	0·06

The base-exchange capacities of the montmorillonite and beidellite mples nos. I, II, III, VI were determined by Dr. R. K. Schofield[2] and e results recalculated on the basis of half the dehydrated unit cells

In Marshall's calculations ((13) pp. 438–440) it seems that the sum of the negae charges is listed as cations per unit cell, otherwise, as far as a recalculation of data shows, the fit is too good.

My best thanks are due to Dr. Schofield for these data which were obtained by ew and unpublished method, based on the reduction in the titrateable acidities to 6·75, which is brought about by treating the acid-washed materials with *N*-assium chloride solution.

of the composition given in tables III and IV, i.e. $Si_{3\cdot74}Al_{2\cdot03}Fe_{0\cdot03}$ $Mg_{0\cdot20}O_{11}$ for montmorillonite, sample no. I. In table VI the sum of the negative charges produced, the sum of the valencies of the excess cations and the base-exchange capacities are listed together. The agreement is good, except in the case of the magnesium-beidellite, sample no. VI where the exchange capacity is much too low. It is possible that this low result is connected with the fact that sodium is the main exchange ion in this case, but work on this question will be continued. In all other cases it seems that the excess cations balance the negative charges on the lattice which are due to isomorphous replacements and that they are all exchangeable. This result should be compared with Marshall's (13, p. 446) statement:

'The mono and bivalent bases present in clays thus fall into four categories. (1) Those needed to complete the framework, chiefly Mg replacing Al. (2) Those which partly balance the charge on the framework and are incorporated within it. Mg, K, Na, and Ca may all be present in this non-exchangeable form. (3) Exchangeable cations which also contribute to balancing the charge on the framework, but which are situated between the layers and are there associated with water molecules. (4) Cations of the electrical double layer surrounding the particles.'

The new result represents a considerable simplification of Marshall's statement, his categories 1 and 3 are retained, but category 2 is rejected and 4 arises from and is included in 3.

It has been mentioned above that for the calculation of the middle aluminium layer two possibilities of replacing aluminium by magnesium exist, the ratio Mg to Al can be either 1:1 with an increase in the negative charge, or 3:2 without increase in charge. If for a given material the excess cations balance the negative charges for one method of calculating the middle layer, the balance remains if the other method is used, but the total sum of excess cations or charges will be different. The ratio 1:1 has been used, because in this case the base-exchange capacities give the same value as the excess cations for montmorillonite and beidellite, samples I to III. It seems also that in micas there is a strong tendency for the number of cations in the middle layer to be either two or three, or very nearly two or three, but not any intermediate value (Holzner (25), Niggli (26)). It must be repeated, however, that these calculations are at present hypothetical and only justified by the fact that the results seem reasonable.[1] They are compatible with, but

[1] When better dehydration curves are available it will be necessary to consider the possibility that the negative charge on the lattice is reduced by a $O'' \rightarrow OH$ transformation. This seems to account for the analyses of certain micas. Brammall (23).

t proved by, the X-ray evidence, and would give the following
ture.

The three-layer lattice has a certain amount of aluminium ions
placing silicon ions in four-co-ordination. In the muscovite structure
ery fourth silicon is replaced by aluminium. In the montmorillonite
oup one out of six is the upper limit for published analyses and one
t of forty the lower one. The middle layer has the ideal compositions
either $2Al^{\cdots}$ (montmorillonite), $2Fe^{\cdots}$ (nontronite), or $3Mg^{\cdot\cdot}$ (magne-
m-beidellite), and $Li^{\cdot}$ or $Ca^{\cdot\cdot}$ ions can replace those three ions to a
all extent. How far mixtures of the three end-members occur is not
t known. The negative charges due to the various replacements are
lanced by cations, which are held on the outside of the three-layer
its and which are exchangeable. This result would confirm and
tend a rule proposed by van der Meulen (24), that the amount of
minium replacing silicon in four-co-ordination is a measure of the
change capacity, but it is believed that a further condition is that the
lancing ions are accessible.

X-ray data.

Hofmann (11, 22) and collaborators have suggested an atomic arrange-
nt for montmorillonite, which is identical with the pyrophyllite
ucture, as far as the three-layer units are concerned. These units are
arated by gaps which are filled with water and vary in size according
the moisture content of the sample. Apparently the layers are all
rallel and equidistant without further orientation. The powder
gram consists of a series of reflections from the basal spacing plus
ss-grating spectra due to the hexagonal arrangement of the three-
er unit. Nontronite and beidellite are said to have the same structure,
d these results are confirmed with minor modifications (monoclinic
against rhombic unit cell) by Gruner (9). Gruner's X-ray data for
ntronites show, however, considerable differences for different samples,
d, on the whole, too many lines. Accurate data for beidellite do not
m to have been published anywhere. Kerr (15) states that the
gnesium-beidellite from Hector, California, gives the same powder
gram as nontronite, but he records no spacings larger than 4·5° Å.
X-ray powder diagrams of the air-dry minerals listed in table I were
en with copper and iron radiations. Technical details have been
en in previous communications (18). The results are given in table VII,
d some of the diagrams in plate V. All materials give the same type

TABLE VII. X-ray powder diagrams of minerals I to VI, taken with copper and iron Kα radiations.

	I.		II.		III.		IV.		V.		VI.		Indices according to (22) or marked ?
1.	15·3	*vs*	15·1	*vs*	15·2	*m*	15·4	*vs*	15·6	*vs*	15·8	*s*	(001)
2.	5·15	*s*	5·03	*s*	5·05	*w*	—		—		—		(003)
3.	4·50	*vs*	4·45	*vs*	4·51	*vs*	4·56	*vs*	4·55	*vs*	4·57	*vs*	(110) (020)
4.	—		—		3·36	*w*[1]	—		—		—		—
5.	3·07	*vs*	3·02	*vs*	3·03	*w*	3·11 / 3·03 [2]	*vw*	3·11 / 2·98	*vw*	3·23 / 3·08	*w*	(005
6.	2·61 / 2·55 [2]	*vs*	2·60 / 2·49	*vs*	2·60 / 2·54	*vs*	2·64 / 2·56	*s*	2·62 / 2·56	*s*	2·65	*s*	(130 (200)
7.	2·41	*w*	2·38	*w*	2·38	*w*	2·43	*w*	—		2·48	*m*	(006) ?
8.	2·240	*vw*	2·240 / 2·164	*vw*	2·240	*vw*	—		—		—		—
9.	2·155		2·090		2·140		—		—		2·285	*vw*	(220) (040)
10.	1·905	*vw*	1·890	*vw*	—		—		—		—		(007) ?
11.	1·708 / 1·682	*m*	1·694 [3] / 1·654	*m*	1·700 [3] / 1·640	*m*	1·715	*w*	1·716	*w*	—		(008) ?
12.	1·497	*vs*	1·488	*vs*	1·500	*vs*	1·668	*w*	1·668	*w*	1·748 / 1·689 [3]	*m*	(240) (310)
13.	1·292	*m*	1·284	*m*	1·302 / 1·285	*w*	1·518	*vs*	1·519	*vs*	1·527	*vs*	(150)
14.	1·247	*m*	1·241	*m*	1·245	*w*	1·318 / 1·300	*vw*	1·316 / 1·300	*w*	1·320 / 1·301	*s*	(330) (060)
15.	0·970	*vw*	0·970	*vw*	—		1·258	*vw*	1·266 / 1·246	*w*	1·267	*vvw*	(260) (400)
16.	0·863	*vw*	0·862	*vw*	—		—		—		0·990	*w*	(0.0.12) ?
							—		—		0·878	*w*	(350) (170) (420)
a...	5·17Å.		5·14		5·17		5·23		5·23		5·24Å.		(190) (460) (530)
b...	8·98Å.		8·93		9·00		9·11		9·11		9·16Å.		(390) (600)

[1] Probably quartz line.

[2] Edges of broad line.

[3] Separated into two lines, when iron radiation is used.

powder diagram, but there are slight differences with regard to sitions and intensities of lines.

The differences in position of the lines can be summarized by using ofmann's indices (060) and (400) for the lines nos. 12 and 13 to calculate e length of the axes a and b of the unit cells. The figures are given table VII and are compared with the corresponding figures for the droxides of aluminium and magnesium and for talc and pyrophyllite table VIII.

TABLE VIII. Length of a and b axes of various minerals in Å. units.

	Montmorillonite.	Nontronite.[1]	Mg-Beidellite.
a	5·15	5·23	5·24
b	8·95	9·11	9·16
	Hydrargillite.	—	Brucite.
a'	5·06	—	5·38
b'	8·62	—	9·36
	Pyrophyllite.	—	Talc.
a	5·14	—	5·26
b	8·90	—	9·10

The differences in the intensities of lines affect the higher orders of basal spacing, mainly the lines nos. 2 and 5, which are very weak absent, if iron or magnesium replace aluminium in the structure. The lacement of silicon by aluminium does not seem to affect the powder gram in any way; the diagrams of samples nos. I and II are almost ntical.

The magnesium-beidellite diagram shows also another peculiarity. hereas the lines nos. 13 and 14 have about equal intensity in all other mples, no. 13 is strong and no. 14 very weak for the magnesium-idellite.

Lattice Shrinkage.

All six materials investigated show reversible lattice shrinkage upon hydration. From the position of the first order reflection of the basal acing the following values are obtained:

at 50 % relative humidity	15–15·5 Å.
at 110° C.	12–12·5 Å.
at 300° C.	about 10 Å.

These values are not very accurate, but they are correct within 5 %. e loss upon ignition on material in equilibrium with an atmosphere 50 % relative humidity was determined on small samples of all

[1] Similar values for nontronite are reported by J. W. Gruner (9).

minerals except the nontronites, where the few milligrams of material at my disposal were insufficient for this determination. The values are:

	I.	II.	III.	VI.
Ignition loss as per cent. of air-dry sample ...	23·1	19·6	17·7	24·1

The water in montmorillonite is believed to enter between the three-layer units in the form of sheets of spheres in close-packing. It regulates, therefore, the basal spacing, and changes in the water content cause the reversible lattice shrinkage and expansion. The intensities of the higher orders of the basal spacing are strongly affected by the water content. Our data, given in table VII, show that the intensities of the higher orders of the basal reflection for a *given* water content vary also according to the composition of the middle layer.

Calculations showing the effect of change in water content have recently been made by Bradley, Grim, and Clark (19) and by Maegdefrau and Hofmann (22). These authors assume two layers of water to be present between the three-layer units for material with a basal spacing of about 15 Å. No values for structure factors or other details of calculation are given in either paper, but the X-ray methods are different, and presumably different formulae are used for the decrease of the intensity with increasing angle θ. The values of these authors for (001), (003) and (005) are given in table IX.

Table IX. Calculated and observed intensities for (001), (003), and (005) for montmorillonite, given by Maegdefrau and Hofmann (for powder line) and by W. F. Bradley, R. E. Grim, and C. L. Clark (crystal plane reflection).

	Maegdefrau and Hofmann		Bradley, Grim, and Clark.	
	Calc.	Obs.	Calc.	Obs.
(001) ...	160	>5	22·3	*vs*
(003) ...	3	1	2	*m*
(005) ...	8	2	15·8	*vs*

In order to see how these intensities are affected if all the aluminium in montmorillonite (2Al) is replaced by magnesium (3Mg) as in magnesium beidellite, or by iron ($2Fe^{\cdots}$) as in nontronite, rough intensity calculations were made assuming equal scattering power for O'', OH', and H_2O and using Bragg and West's empirical F values (21). These calculations were made for the case of a powder line on a cylindrical film (*a*) and for the case of a crystal plane reflection (*b*). The results are shown in table X where the intensity of (001) for montmorillonite (2Al) is made equal to the values given by Maegdefrau and Hofmann (22) (*a*), and by Bradley, Grim, and Clark (19) (*b*).

TABLE X. Calculated and observed intensities for (001), (003), and (005) for montmorillonite (2Al), nontronite (2Fe$^{\cdots}$), and magnesium-beidellite (3Mg), (*a*) for powder line, (*b*) for crystal plane reflection.

		2Al		2Fe		3Mg	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
(*a*)	(001)	160	*vs*	376	*vs*	234	*vs*
	(003)	2·8	*s*	0·19	—	0·75	—
	(005)	22·3	*vs*	34·3	*vw*	26·4	*w*
(*b*)	(001)	22·3	*vs*	51·8	*vs*	32·1	*s*
	(003)	1·2	*s*	0·08	—	0·32	—
	(005)	15	*vs*	23·2	*vw*	17·9	*w*

The effect of the substitution works in the right direction and is reasonably strong for (003), where it could explain the observed intensities, but the agreement is not too good for (005), where the observed intensities decrease very much, whereas the calculated ones increase or decrease very little, if equal (001) intensities are taken as a basis of comparison. More data are needed before definite conclusions can be drawn from these observations.

The results of the X-ray data confirm the hypotheses put forward under the heading of isomorphous replacements in so far as they show the samples I to VI to belong to the same general structural type. The whole group is, accordingly, best represented in a ternary diagram with the end-members montmorillonite, $Al_2Si_4O_{11}$ (A), nontronite, $Fe_2Si_4O_{11}$ (B), and magnesium-beidellite $Mg_3Si_4O_{11}$ (C) if the completely dehydrated formulae are used. Iron-free beidellite would coincide with A although the ratio of silica to alumina is different. In fig. 1 the six samples investigated are plotted in this way together with a few beidellites, ratsihite, and attapulgite. Attapulgite belongs to this group according to Kerr (15), but this is contradicted by Lapparent (16), who finds that this material has a basal spacing of 10·2 Å. The field for beidellites is also indicated, based on Larsen's data. It would perhaps be better to have a new name for C instead of magnesium-beidellite and to call all members of the group beidellites. It is possible that other beidellites in this sense along the BC line occur among saponites and bowlingites (17). How far minerals corresponding to points in the interior of the triangle exist cannot be said at present.

It seems that all members of the group are subject to fairly large isomorphous substitutions leading to a negative charge on the lattice of 0·5 units per $R_2Si_4O_{11}$, if R_2 stands for 2Al, 2Fe$^{\cdots}$, 3Mg, as elaborated above. This would correspond to exchange capacities of the order of 100 milli-equivalents for 100 grams of air-dry material. The excess

cations are able to hold loosely large amounts of water which govern the basal spacing. The ideal end-members mentioned above have no substitutions, no negative charge, no excess cations, and therefore no loosely held water. They belong to a different structural type, the pyrophyllite-talc type (compare p. 141). This seems to be the reason why

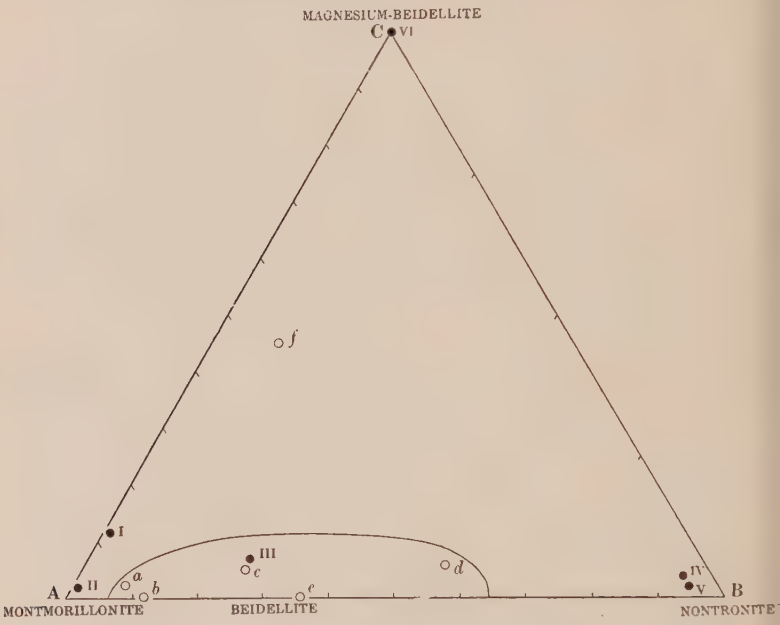

FIG. 1. Ternary diagram of the montmorillonite group. Points I–VI correspond to the six samples investigated; *a* to *d* to other beidellites; *e* to faratsihite; and *f* to attapulgite.

all montmorillonites, beidellites, and nontronites contain appreciable amounts of magnesium and calcium, a fact which has led to conflicting opinions in the literature. Lapparent (16) believes that the montmorillonite structure contains $SiMg(OH)_6$ layers alternating with the usual three-layer units, in analogy with the structure of the chlorites. But this seems not to take into account the reversible lattice shrinkage. With a basal spacing of 10·2 Å. corresponding to montmorillonite heated to 300° C. there would be no room for this group. In a recent classification of clay minerals Lapparent (20) puts the beidellites tentatively into the kaolin group. This also does not agree with the data given in this paper.

Montmorillonite heated to 300° C. and pyrophyllite give powder iagrams which show very large differences.[1] Their structures are upposed to be identical except perhaps for lack of orientation of the uccessive three-layer units. This lack of orientation may be due to the omparatively large amount of isomorphous replacement in the lattice hich would prevent a regular three-dimensional lattice arrangement, ut the possibility cannot be excluded that the structure of montmoril- nite is altogether different from the one proposed by Hofmann.[2] His dmittedly rough intensity calculations for the (*hk*0) lines (22, p. 316) how large variations upon replacement of aluminium by iron or iagnesium, contrary to the observed facts. He has, therefore, to intro- uce several additional hypotheses in order to make these calculations t the experimental data. It still seems that the experimental evidence insufficient to prove or disprove his structure which certainly is a very seful first approximation, and has been used as a basis for discussion this paper.

In conclusion, the author wishes to thank Sir William Bragg and the anagers of the Royal Institution for laboratory facilities at the Davy araday Laboratory, where part of the X-ray work was carried out, nd Dr. E. M. Crowther for his help in the preparation of the manuscript.

Summary.

A classification of some clay minerals is made according to their ttice structure, and to the quality of their powder diagrams. The nportance of the latter criterion is emphasized.

The montmorillonite group is shown to have three end-members, ontmorillonite, $Al_2Si_4O_{11}$, nontronite, $Fe_2Si_4O_{11}$, magnesium-beidellite, $Mg_3Si_4O_{11}$. The formulae given correspond to the completely dehydrated nd-members, free from isomorphous replacements.

One montmorillonite, two beidellites, two nontronites, and one iagnesium-beidellite are studied in detail. Their isomorphous replace- ents are calculated on the basis of eleven oxygen atoms and the excess ations are found to balance the negative charges resulting from the eplacements. Similar calculations with the same result have previously een made by Marshall. Base-exchange determinations on three of

[1] For this reason we do not think that Bradley, Grim, and Clark's terminology f first, second, and third hydrate of pyrophyllite for montmorillonite at various tages of hydration is satisfactory.

[2] It is, for example, possible to keep the silicon-oxygen framework unchanged nd to distribute the aluminium ions over the four-co-ordinated spaces of the iddle layer.

these materials show that all excess cations are exchangeable, but that in the case of magnesium-beidellite there are discrepancies, which require further investigation.

The hypothesis is made, that a certain amount of isomorphous replacement of silicon by aluminium and perhaps of aluminium by magnesium is essential for this structural type and may explain both the high water content, which is due to the excess cations, and the poor diffracting power for X-rays, which is due to the lack of regularity of the lattice.

Dehydration data given in the literature are discussed and the lack of agreement for the amount of hydroxyls given in the usual formula $Al_2Si_4O_{10}(OH)_2$ is pointed out.

X-ray powder data for the six samples and values for the lattice shrinkage upon dehydration are given. They show all samples to belong to the same structural type. The replacement of aluminium by iron and magnesium within the lattice causes an increase in the lattice dimensions and for air-dry material a decrease of the intensities of (003) and (005). Rough intensity calculations on the basis of Hofmann's montmorillonite structure (22) show corresponding values for (003) but too high values for (005), and the need for further experiments is pointed out.

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Since going to press, X-ray diagrams of two samples of attapulgite (p. 151), kindly nt by Professor J. de Lapparent, show this material to be distinctly different om montmorillonite and not to show the characteristic lattice shrinkage.

Explanation of Plate V.

X-ray powder photographs of clay minerals of the montmorillonite group and of rophyllite.

Fig. 1. Pyrophyllite.
Fig. 2. Montmorillonite.
Fig. 3. Magnesium-beidellite.
Fig. 4. Magnesium-beidellite.
Fig. 5. Nontronite.

Figs. 1 to 3 were taken with Cu-K_α and figs. 4 and 5 with Fe-K_α radiation. The ensities in the centre have been reduced through partial shading in making the nts.

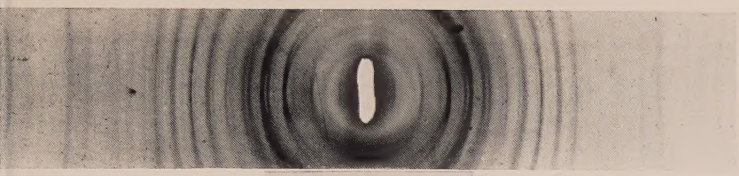

Fig. 1. PYROPHYLLITE

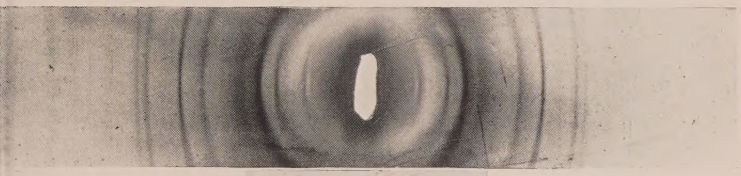

Fig. 2. MONTMORILLONITE

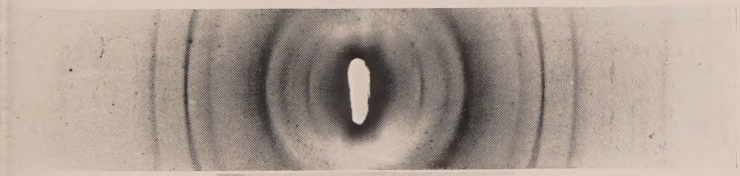

Fig. 3. MAGNESIUM-BEIDELLITE

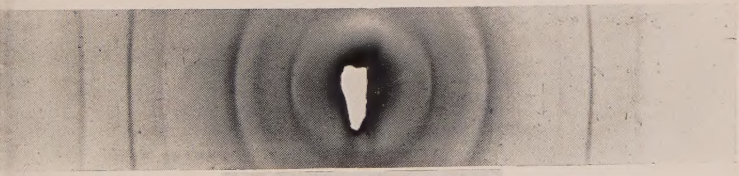

Fig. 4 MAGNESIUM-BEIDELLITE

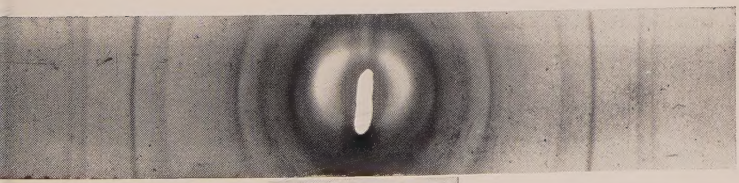

Fig. 5. NONTRONITE

G. Nagelschmidt: X-ray photographs of clay minerals.